Second Quarterly Report

for

Solar Cell Contact Development

Contract No.: NAS 5-11595

Prepared by

Applied Science Division
Litton Systems, Inc.
2003 East Hennepin Avenue
Minneapolis, Minnesota 55413

for

Goddard Space Flight Center

Greenbelt, Maryland

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(28 Sept. 1968 - 28 Dec. 1968)

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Prepared by:

Applied Science Division
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Project Manager: Richard Jacobson

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SUMMARY

This report describes the technical work performed during the second quarter of a 12-month research contract, No. NAS 5-11595, for NASA-Goddard Space Flight Center. The contract objectives are twofold: (1) to identify the Ti-Ag contact degradation mechanism on Si solar cells and (2) to determine whether sputter deposition of contact material is compatible with present solar cell configurations. Contract effort during this second reporting period was again concerned with contact degradation studies.

The first quarter technical results indicated that contact degradation occurs within the Ti-Ag contact and is most probably due to a chemical transformation of the highly reactive Ti metal to a stable compound of Ti such as, for example, an oxide or nitride. One of the objectives of the second quarter was to determine the reactivitiy of Ti to various gases and aqueous solutions when unprotected and when coated with an evaporated film of Ag. Gases include non-purified and purified Ar, wet Ar, wet and dry O_2, forming gas, and N_2. Aqueous solutions include NaOH, KOH, NaCl, and H_2O. Results of this work clearly show that, under certain conditions, diffusion of species through the Ag film does occur and results in the attack of the underlying Ti. Blistering and/or peeling of the Ag overlayer was observed in some cases. Controlled environmental tests were also conducted on Si solar cells with the result that blistering was promoted.

Auger spectroscopy has successfully identified contaminants in Ti-Ag contacts. In one cell, Cl or B was noted while O was found in another. Sectioned cells were investigated by the Electron Mirror Microscope and by potential probe experiments. Nothing particularly unusual was observed here.

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SECTION I

Introduction

Background.— The Ti-Ag contacts presently employed on Si solar cells are known to degrade in storage. Degradation is noted by the reduction in power efficiency of individual solar cells or of an array of cells as found on solar cell panels. The basic problem appears to be due to separation of the Ti-Ag contact from the underlying Si which manifests itself by blistering and/or peeling. Electrical performance is reduced by the corresponding increase in internal resistance of the solar cell.

The objective of Task 1 of this contract is to identify the cause of Ti-Ag contact degradation and to recommend to the industry guidelines for fabricating non-degrading contacts for Si solar cells. Work during the first quarter gave some important results. It was found that contact separation occurs within the Ti-Ag contact and generally close to the Ti-Ag interfacial region as observed optically and from electron microprobe data. Further, the interfacial region exposed by intentionally peeling cells invariably exhibited discoloration in the form of interference colors and staining and suggests the existence of possible oxides, nitrides, or hydrides of Ti. The electron microprobe detected Ti in the contact although x-ray examination did not reveal Ti in its normal crystalline state nor any sufficiently well-crystallized compound of Ti.

Scope of Work - Second Quarter.— During the second quarter

1) additional optical studies were performed on solar cells received from NASA-Goddard Space Flight Center,

2) heat treatments were conducted on Ti and Ag on Ti test samples in various gas ambients,

3) test samples of Ti on Si, Ti-Ag on Si, Ag on Ti, and solar cells were exposed to various aqueous solutions,

4) Auger measurements were performed on a solar cell whose contact was stripped by sputtering and also on a peeled cell,

5) sectioned cells were looked at with the Electron Mirror Microscope (EMM), and

6) potential probing was done on a sectioned cell.

(a)

(b)

Ex. 1

θ^2

SECTION II

Technical Discussion

Optical Inspection.— Additional Si solar cells were received from NASA-Goddard and optical investigation of these cells was undertaken using the Reichert Optical Microscope. These cells exhibited several distinct features not previously observed on cells reported in the First Quarterly Report. First, a transparent substance in the form of a finger-like structure was evident on the Ti-Ag grid lines. Second, blisters were frequently observed on the Ti-Ag contacts.

The finger-like structures were not observed on the initial cells studied and therefore it was of interest to determine their origin. Figure 1a is a micrograph showing these structures. Texas Instruments, the manufacturer of these cells, indicated that the SiO antireflection layer was evaporated directly onto the Ti-Ag grid lines without the use of a mask. The ohmic strip contact is, however, masked. It is further observed from Figure 1a that the finger-like structures are found only in the unmasked areas (grid lines). It is evident that these features are due to SiO on the grid lines. It is not clear why or when the SiO assumes this structure, i.e., during evaporation or later. A brief immersion of a solar cell in HF acid dissolves the SiO antireflection layer found on the Si and also removes the finger-like structure on the Ti-Ag contacts.

An example of a blistered contact is shown in Figure 1b. Blisters are dome shaped and generally have a near-circular cross section. Their isolation suggests that they are caused by isolated events. One very likely cause of blisters is the development of a gas bubble within the Ti-Ag contact which eventually causes the contact to heave. Blistering is frequently observed with paints (generally due to trapped water vapor) and in the corrosion of metals (liberation of a gas such as hydrogen). The grain-like structure noted in Figure 1 is believed due to single crystal grains of Ag separated by grain boundaries--contrary to what was initially thought and reported in the First Quarterly Report.

If the observed blisters are caused by gas bubbles which force the contact to lift, then the blister might be expected to rupture or at least grow in size when exposed to vacuum. Experiments were performed on several cells for the purpose of observing any significant change in a blistered contact. The initial results were negative. Additional experiments are planned in the near future to look for minor changes in blister size.

Heat Treatments.— The purpose of conducting heat treatments on Ti and evaporated Ag on Ti test samples was to determine the reactivity of Ti to various gases and to evaluate the protection action of an evaporated film of Ag when applied to Ti. It was also of interest to note if blistering develops. Test samples of Ti were prepared from ∿ 10 mil thick Ti foil shaped to dimensions 1/4 in. x 5 in. A Ag film of ∿ 1 μ thickness was evaporated on one side of some Ti samples. Prior to this evaporation, the Ti was etched in hot 30% HNO_3-2% HF solution to remove the oxide. Because the Ti was subsequently exposed to air prior to Ag evaporation, a very thin oxide film is nevertheless present. In one case a visible but yet thin oxide film formed on Ti during the evaporation run. The results of the heat treatments are not thought to be seriously affected by the thin oxide layer.

Heat treatments were carried out using a tube furnace and quartz tube. Gas was passed through the quartz tube at a low flow rate. Test samples were first admitted to the cool region of the tube outside of the furnace and sufficient time allowed for the system to purge (10 min) before samples were moved to the hot zone. Samples were placed near the end of the furnace where a large temperature gradient exists. In this way the reactivity of Ti could be evaluated for temperatures ranging from∿200 to 800°C in a single run. Temperatures were initially determined by a thermocouple. The temperature measurements are only approximate because of their sensitivity to experimental conditions. In all cases the heat treatments were conducted for 10 min.

Gases employed include dry Ar, dry and de-oxygenated Ar, wet Ar, dry and de-oxygenated N_2, dry and de-oxygenated forming gas (90% N_2, 10% H_2), dry O_2, and wet O_2.

Heat treatments on Ti gave the following general results. Both O_2 and water vapor (wet Ar) are highly effective in oxidizing Ti. The oxide was readily apparent by the development of interference colors at temperatures above about 400°C. Oxidation is known to occur at lower temperatures but in this case the limiting thickness of the oxide film is less than that required for interference colors (∿ 1000 Å) and hence the film cannot be observed optically. Relatively thick oxide films formed at temperatures above about 600°C were grey in color. Dry and de-oxygenated Ar, N_2, and forming gas did not produce significant discoloration of Ti for temperatures up to 800°C although N_2 and forming gas did produce a slight yellow appearance to Ti at temperatures above 500°C. Initial experiments demonstrated the importance of using both dry and de-oxygenated gases, because only a trace amount of water vapor or O_2 caused oxide growth on Ti.

Heat treatments on evaporated Ag on Ti samples gave some interesting results. In purified Ar a test sample lost its silver-like appearance at temperatures above ~ 500°C. Below this temperature the silver-like appearance remained. Apparently Ag diffused into Ti at the high temperatures. Similar results were obtained in N_2. In forming gas the Ag became darkened in the extreme hot zone (700-800°C). In dry oxygen, on the other hand, the Ag film retained its silver-like appearance and took on a grain-like appearance in the extreme high temperature zone. When the Ag film was removed by nitric acid, interference colors were found on the Ti. They correspond in position to the interference colors developed on the opposite uncoated face. This result shows then that oxygen readily penetrates the Ag film at temperatures above 400°C and results in oxidation of the underlying Ti. Oxygen penetration very likely occurs at lower temperatures but it could not be observed in these experiments because of the limited oxide thickness. In wet Ar the Ag film partially protects the underlying Ti from oxidation as inferred from the displacement of interference colors between the front and back face. This finding suggests that diffusion of water vapor through Ag proceeds at a lower rate than oxygen diffusion. The Ag film in wet Ar becomes slightly discolored below 600°C and grey in appearance in the extreme high temperature region (600-800°C). Results for wet O_2 were similar to dry O_2 except that large blisters developed at high temperatures (600-800°C).

Several double heat treatments were conducted for the purpose of noting conditions for the development of blisters. Blisters were observed by heat treating first in dry O_2 and then in forming gas. Interestingly, the blisters developed only in the region where the interference color bands were located (400 to 500°C). Blisters were not observed when the films were heated first in forming gas and then in wet O_2 or first in dry O_2 and then in wet O_2. The latter case did, however, show small regions where the Ag film apparently broke loose or erupted, thereby exposing colored spots of the underlying titanium oxide.

In summarizing the main results of this study, we find that both O_2 and water vapor readily react with titanium to form visible oxide films at temperatures above about 400°C and that O_2 and, to a lesser extent, water vapor penetrate througha thin Ag film at these temperatures. O_2 or water vapor penetration at lower temperatures cannot be ruled out from these experiments because the limiting thickness of the oxide formed at these temperatures ($<$ 400°C) does not produce interference colors. Blisters similar to the type observed on solar cells were observed by first heat treating in dry O_2 and then in forming gas. The

conclusion reached by these results provides some insight into the reactivity of Ti and the porosity of a thin Ag film. However, the results do not readily explain the normal degradation of Si solar cells which proceeds at or near normal temperatures. The time scales differ by orders of magnitude (10 min vs several months or more) and this may possibly close the gap. In search of alternate explanations various test samples were exposed to different aqueous media and some rather interesting observations were made. These are now reported.

Exposure to Aqueous Media.— Test samples included Ti and Ag-on-Ti samples similar to those used in the heat treatments and, in addition, samples of evaporated Ti on Si, evaporated Ti-Ag on Si, and Si solar cells having Ti-Ag contacts. Si substrates on which Ti and Ti-Ag were evaporated were boron doped 1 to 40Ω-cm Si wafers obtained from Monsanto. The Ti-Ag on Si samples were prepared by a double evaporation process, i.e., by first evaporating a thin film of Ti and subsequently evaporating Ag without exposing the wafer to the atmosphere. The circular Si wafers were cleaved in order to obtain several test samples per wafer.

In one experiment, Ti on Si, Ti-Ag on Si, and Ag on Ti samples were placed on a glass pedestal within a glass beaker partially filled with double distilled water. With the samples above the liquid level, the water was heated with a hotplate to $\sim$80°C. The beaker was covered to prevent loss of water and allowed to run for several days. Similar test samples were placed in a second beaker and heated to approximately the same temperature, only in this case no water was used. The former case corresponds to a high relative humidity atmosphere and, in fact, water vapor was found to condense on the test samples. A comparison of the results of these two treatments was striking. In the high humidity case the Ti-Ag on Si sample exhibited blisters and the Si was attacked somewhat. Samples in the beaker without water showed no change in physical appearance. The effect of water vapor (or possibly trace impurities in the water) on the deterioration of the metal films is clearly evident here and was expected on the basis of solar cell degradation studies at NASA-Goddard.

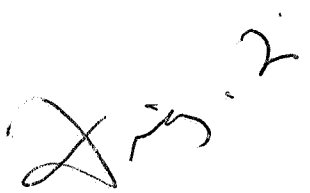
Test samples of Ti on Si and Ti-Ag on Si were placed in concentrated solutions of KOH, NaOH, and NaCl at room temperature. Within approximately 1 hr, blisters were found to develop on the Ti-Ag on Si sample immersed in KOH. The Ti-Ag film also showed evidence of peeling at the edges adjacent to the Si. Similar results were obtained on Ti-Ag on Si samples in NaOH,

except that the reaction rate was less by a factor of about 10. Blisters also developed in the NaCl solution and the reaction rate was even less than in NaOH. Both KOH and NaOH attacked Si somewhat, i.e., slowly dissolved it. The Ti stripped from the Si when placed in KOH and NaOH and the Ti film became relatively transparent when left in solution for several hours. The Ti is either oxidized and/or dissolved slowly when placed in these solutions. This was not the case in NaCl.

Blistering was more severe at the sample edges where peeling often occurred and therefore it was important to note if blisters develop when edge effects were eliminated. An experiment was performed where a Ti-Ag on Si sample was coated with apiezon wax except for a small area on the Ti-Ag contact. This sample was then placed in KOH and blisters developed in the unprotected region. On removing the wax it was observed that blisters were evident only in the unmasked area as shown in Figure 2. This shows that edge effects are not essential for blistering. It is, on the other hand, apparent that some specie (such as hydroxyl ions in KOH or NaOH) is capable of penetrating through the Ag film or defects thereof and corrodes the underlying Ti layer. The corrosion probably liberates gas (possibly hydrogen) to form blisters. This then is one example where blisters develop at room temperature.

The action of the salt solution is not clear. It is known, however, that a salt spray (such as found near the ocean) is a corrosive atmosphere. Iron, for example, is known to corrode at an accelerated rate when placed in such an environment. The corrosion of iron and, for that matter, corrosion in general is a very complex and an often not well-understood phenomenon. Several good references on corrosion are available.[1-3]

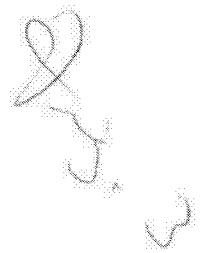
To verify that aqueous solutions of NaOH, KOH, and NaCl are corrosive to Ti, samples of Ti were immersed in KOH and NaCl at room temperature. The corrosive nature of KOH became apparent after several hours by the formation of interference colors which later developed into a dark surface film as the film thickness increased. Color bands yet remained in the vicinity of the liquid level and appeared similar to the oxide film formed by heat treatment in O_2 and water vapor. The large film thicknesses achieved in KOH suggests that these films are either more porous than oxide films formed by heat treatment or the film growth mechanism is completely different. Possibly hydroxyl ions may be responsible for this difference. Ag test samples exhibited no visible corrosion in KOH. Also, no corrosion films were apparent on Ti and Ag when left in NaCl solution for several days.



Galvanic corrosion often is active when two dissimilar metals are in electrical contact with each other when exposed to an electrolyte. A current flows from one metal to the other (so-called galvanic current) and provides a driving force for corrosion. To evaluate what effect galvanic corrosion might have on a Ti-Ag couple, a test sample of Ti and Ag was placed in both KOH and NaCl and in each case the dissimilar metals were electrically shorted externally. The corrosion results were similar to those described above and therefore galvanic corrosion does not appear to play a significant role here.

At this point it was of interest to note if the various electrolytes (KOH, NaOH, NaCl) might promote blistering on Si solar cell contacts just as observed on the test samples. One significant difference between the Ti-Ag test samples and the solar cells is the thickness of the Ag overlayer. The thickness of the Ag film on the test samples was $\sim$ 1 μ while $\sim$ 5 to 10 μ on solar cells. Solar cells for this study were carefully selected in order not to include cells with blisters initially present. A few selected areas of each of four cells were initially photographed and subsequently were placed in solutions of KOH, NaOH, NaCl, and distilled H_2O--all at room temperature. Cells were removed from solution after 3 and 10 days for optical inspection and photographing. The results are now summarized.

Blisters were found to develop in KOH, NaOH, and NaCl but not in distilled water. A three-day exposure was already sufficient to form blisters and after 10 days these blisters generally grew in size while new blisters developed. This can be seen in Figure 3 where a micrograph of a selected area of a cell is shown after 3 days (3a) and 10 days (3b) exposure to NaCl solution. The dark regions are blisters and result from low reflectivity under normal incident illumination. The upper region of the contact of Figure 3b is beginning to peel and more severe peeling was observed in other regions of the cell. Micrographs of a cell placed in KOH are shown in Figure 4. Figure 4a was taken initially and 4b after a 3-day exposure. Both KOH and NaOH were found to dissolve the SiO antireflection film (compare Figure 4a with Figure 4b) and Si itself. After 10 days these two solutions had etched the cells to the extent that the dimensions of the Si were noticeably reduced and the contacts separated from the Si. This was not the case in NaCl, i.e., no visible attack of the SiO or Si was observed. In fact, in many respects the NaCl attack is very similar to normal degradation observed on solar cells. We do not wish to imply that normal solar cell degradation is necessarily caused by NaCl found in the atmosphere, but it certainly is a possible



contributor. In addition, the fact that KOH and NaOH seriously attack Si and SiO does not necessarily imply that these agents or possibly the hydroxyl ion itself must be ruled out. Considerably more information needs to be derived such as: (1) how does degradation depend on the concentration of these corrosive agents, or (2) what other corrosive agents found in the atmosphere cause degradation (e.g., S, SO_2, NH_3, F_2, Cl_2, Br_2). On the other hand, it is evident that degradation very likely proceeds by corrosive agents that penetrate through the Ag film and react with the underlying Ti. Blisters develop by liberation of gas in the form of by-products of the corrosion process.

Auger Spectroscopy Studies.— Some initial results of Auger electron spectroscopy measurements on an RAE Si solar cell were reported in the First Quarterly Report and a description of Auger measurements was given. At that time the solar cell had been only briefly sputtered with Ar in the uhv system to clean the cell. Auger spectra showed Ag present as expected (Auger peaks at 77, 264, 300, and 357 eV), a small amount of Si (90 eV), and weak Auger peaks at 127 and 183 eV. Some Si is believed to be backscattered to the contact during sputtering by Ar gas scattering. The Auger peak at 183 eV is believed due to either Cl or B. The origin of the 127 eV peak is not known. No Ti was found.

This quarter the same cell was sputtered in situ an additional number of times and the contact was eventually sputter-removed. The Ar energies used in sputtering were 150 eV (accumulative time of 1/2 hr) and 250 eV (accumulative time of 2 hr 40 min) at a current density of $\sim$0.1 A/cm^2. Auger spectra were recorded after each sputter treatment. In many respects the results of this investigation developed as expected, i.e., Ag was the major Auger peak during most of the sputter-stripping treatments and only when the contact became very thin did Ti become the predominant peak. Subsequently Si became predominant. The most unexpected result was the behavior of the Auger peak at 183 eV. This peak was noted throughout the stripping process but only developed to its fullest extent after an incubation period after sputtering. The peak was absent just after sputtering and gradually developed over a period of several hours. It was initially thought that the 183 eV peak was due to contamination from the background gas (e.g., Cl_2) or possibly contamination from the electron gun. A close examination found, however, that the development of the 183 eV peak was independent of the time of exposure to the electron gun and the vacuum environment. Furthermore, no evidence of the 183 eV peak was found when Auger spectra were recorded from adjacent Si surfaces.

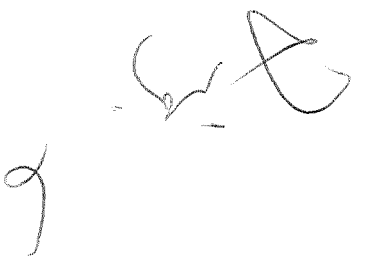
In addition, a similar behavior had not been noted in previous Auger measurements in this system. An alternative explanation is that sputtering with Ar depletes a thin surface layer of this impurity (Cl or B) and subsequently the surface impurity concentration is restored to equilibrium by bulk diffusion. Recent sputtering investigations with Cu-Ni alloys in our laboratory have shown that preferential sputtering can occur and results in a large excess of one constituent over the other. Also, diffusion from the bulk was found to restore the surface concentration to its initial prebombardment state. It therefore seems reasonable that a similar situation is occurring on the solar cell contacts.

An Auger spectrum recorded in the Ag-Ti transition region is shown in Figure 5. Noise problems limited the sensitivity of these measurements to an estimated 1 to 10% detection range. These sensitivities were only realized by using a relatively long time constant in the PAR lock-in amplifier (generally 3 sec) and a slow scan rate in the 0 to 750 V variable scan range. Double and at times triple recordings were made in order to distinguish irratic noise fluctuations from reproducible Auger structure. A typical recording time was 1 hr.

No evidence of O or N was noted in the Auger spectra of the sputter-stripped cell. Unfortunately, hydrogen cannot be detected in Auger spectroscopy.

The RAE-sputter-stripped cell was then removed from the Auger system and inspected optically. Sputter stripping had not removed the Ti-Ag contact completely, i.e., some Ti-Ag remained at one end of the ohmic strip contact. Optical examination found only a light brownish discoloration in the vicinity of the Ti-Ag interfacial region and therefore suggests that this particular cell was only partially degraded.

Subsequently a second cell was placed in the Auger system. In this case the Ti-Ag contact was stripped by mechanically peeling just prior to insertion into the vacuum system which was purged with Ar. The system was then evacuated using a zeolite sorption pump and an ion pump to pressures in the 10^{-8} Torr range without bakeout. The purpose of following this procedure was to avoid grossly contaminating the interface exposed by stripping the contact. Figure 6 is an Auger spectrum of the exposed contact region of the solar cell taken prior to any surface treatment. Reproducibility of several recordings found that Ag is noted at energies of 77, ∿270, ∿300, and 358 eV; Ti at ∿387 and ∿423 eV; and a substantial amount of O at 522 eV.



No Si Auger peak at 90 eV is evident in Figure 6. A very weak but reproducible peak was noted at 183 eV (particularly in Figure 6) and corresponds to the B-Cl peak previously observed on the sputter-stripped cell. It should be noted that the contact to this cell did not strip well in that localized regions of Ag remained on the contact after stripping. Some lateral motion of the sample permitted a (uncontrolled) sampling along a portion of the contact and the unevenly stripped cell was evident by a variation inAg to Ti Auger peaks. In some cases very little Ti was noted. Nevertheless the O Auger peak at 522 eV was always observed and at approximately the same amplitude.

The cell was subsequently given a 150 eV Ar sputtering treatment for 10 min. The resulting Auger spectra were similar to those before sputtering except that some Si was noted on the contact (caused by backscattering as noted earlier). Oxygen was still found in addition to Ag and Ti. Noise difficulties developed at this point and this work was discontinued. On removing the cell and viewing the interfacial region under the Reichert microscope, pronounced discoloration of the interface examined by Auger was found. Discoloration was also noted during the course of this study while the cell was in the vacuum environment.

In summary, Auger Electron Spectroscopy has been successful in identifying contaminants in Ti-Ag contacts, in one case B or Cl and in another case O. Other contaminants could have gone undetected such as H, N (Auger peak reported to lie at 382 eV, i.e., close to Ti), and Na (Auger peak at $\sim$ 990 eV). It is difficult to establish the exact level of contamination from our results without devoting considerable time to calibrate the Auger system for the various elements. Even then it is a difficult problem. Knowing the exact level of contamination is however considered secondary to the actual observation of contaminants here. Needless to say, the Auger results do support our contention that corrosive contaminants (e.g., oxygen, Cl or B, and/or hydroxyl ions) can penetrate through the Ag overlayer and appear at the Ti-Ag interfacial region.

EMM Inspection of Sectioned Cells.— The Electron Mirror Microscope (EMM), being an instrument sensitive to microfields existing at a surface, was used to examine several sectioned solar cells. A brief description of the EMM principle was given in the First Quarterly Report. Sectioning exposes the Ti-Ag contact in depth, the metal-semiconductor junction, and the p-n junction found in the Si. The purpose of this work is to detect any unusual microfield that might exist in the Ti-Ag contact region caused, for example, by IR drops or by dielectric charging. Cells were angle-lapped to $\sim$ 1° of the flat surface

of the cell, the lapped surface being the face with the Ti-Ag grid lines and ohmic strip contact.

Figure 7 shows how the EMM depicts the presence of a p-n junction as found in one of the sectioned cells. In Figure 7A the EMM images the Si surface of the cell with zero cell bias. The fine white lines are caused by polishing scratches. Figure 7b is the same view as (a) but in this case the solar cell is reverse biased 10 V. The p-n junction is clearly visible by the change in contrast about the junction and the white line that runs parallel to the junction. The junction is not perfectly straight and this is caused either by the fact that the junction does have some irregularities or that the exposed surface is not sufficiently smooth or a combination of the two. Figure 7c is the same view with a forward bias of 10 V (0.9 A current). The junction is not as clearly seen as in (b) (slight defocusing in the lower right-hand portion of the figure) because in this case only about 0.7 V of the 10 V develops across the boundary. The voltage difference appears across the internal resistance of the solar cell and external resistance (wires and interconnections).

In Figure 8 the EMM was imaged in the vicinity of a Ti-Ag grid line at the point where it terminates by lapping. Figures 8a, b, and c correspond to zero cell bias, 10 V reverse bias, and 10 V forward bias conditions, respectively. The structure noted in 8a is due to variations in surface topology except for the dark spots which are believed due to dielectric charging (dust particles, insulating compounds, etc.). The jog in the p-n junction in (b) can be due to two effects. First, the contact and immediate surroundings may be raised with respect to the surrounding Si because of a difference in the Ti-Ag to Si lapping and polishing behavior. Second, the jog may be due to doping of the Si by diffusion of contact material. It is believed that the jog is primarily due to the first effect although additional work is required to substantiate this. Any significant voltage drop along the contact and intermediate Si should be revealed by comparing Figures 8a and c. Nothing strikingly unusual is observed here, although there is some difference in contrast. A better method of study is to mechanically pulse the solar cell from zero bias to forward bias conditions and observe the changes in contrast. Various sectioned cells are presently being studied in this manner.

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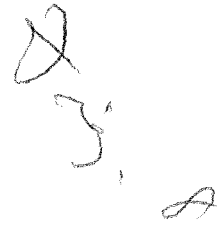

Potential Probing of a Sectioned Cell.— Some potential probe experiments were conducted on a sectioned solar cell for the purpose of detecting any unusual potential profile in the vicinity of a lapped Ti-Ag contact. The cell was lapped in a manner similar to that described in the preceding section. The cell was mounted on a moveable stage driven by micrometer screws. A fine tungsten wire, pointed by electrolytic etching in KOH, served as the probe. A forward current of 1 A was passed through the cell while the tip of a Ti-Ag grid line and the region between the tip and p-n junction was probed, as illustrated in the diagram of Figure 9. The approximate position of the Ti-Ag grid line and p-n junction is indicated here. The probe potential, as shown in the ordinate, was measured with respect to the contact made to the Ti-Ag ohmic strip contact and therefore no significance should be placed on its absolute value. More important is the variation in potential with position. We find on this cell that only a very small IR drop develops along the lapped Ti-Ag grid line, but a rather substantial drop occurs in the bulk Si which lies between the contact and the p-n junction. Here the potential varies approximately linearly with distance, as seen in the more sensitive curve (20X). An abrupt change of $\sim$0.6 V occurs at the p-n junction and is normal under large forward-bias condition. No abrupt potential change occurred elsewhere and therefore no unusual behavior is observed in these measurements. This cell did not exhibit any significant discoloration near the tip of the Ti-Ag grid line and hence it would be of interest to extend these measurements to cells exhibiting degraded contacts.

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SECTION III

New Technology

All the research tools and techniques employed in this study program to date are not new technology developed under this contract and therefore there is none to report here.

SECTION IV

Program for the Next Reporting Period

The program for the third quarter of Contract NAS 5-11595 will very likely include:

1) Additional EMM studies on sectioned cells,

2) Additional potential probe studies on sectioned cells,

3) Initiate Task 3 by depositing Ti and Ag on Si substrates and evaluate their physical and electrical properties and by evaluating the effects of the plasma environment on the p-n junction characteristics,

4) Perform additional analytical studies on degraded cells including the search for contaminants using 3M's electron microprobe, which has a low-element kit,

5) Perform a few selected experiments on degradation of solar cells by corrosive gases and/or aqueous media,

6) Possibly related studies not evident at this time.

SECTION V

Conclusions

It has become increasingly clear that contact degradation can proceed from room temperature penetration of corrosive species through the Ag overlayer in Ti-Ag contacts and that these species react with the underlying Ti, thereby causing chemical and physical changes in the Ti-Ag contact. Blisters are thought to develop by gas liberated during the corrosion process, although this has not been directly confirmed here. However, in a private communication with Texas Instruments, Inc., they reported finding a large amount of hydrogen evolved when blisters ruptured in vacuum. Optical inspection of blistered cells also shows that the origin of blisters appears to lie deep within the contact, that is, in the vicinity of the Ti layer.

The corrosion process is probably complex in that possibly more than one specie may be active. This is seen, for example, by the fact that both alkali solutions of KOH and NaOH and salt solutions of NaCl are effective in degrading Ti-Ag contacts. The detection of Cl or B, and O in Auger measurements also tends to substantiate this fact. Possibly other corrosive agents such as F_2, Br_2, or S may also be effective. It is tempting to speculate that Cl may arise from the salt spray in the atmosphere or possibly from solder fluxes used in mounting solar cells (although most of the cells investigated here were not soldered). Also the alkalis may arise from contaminants in humid environments. Possibly minute quantities of hydroxyl ions found in even pure water may be of a sufficient concentration to cause degradation. Indeed, much work yet remains in order to define more clearly the degradation mechanism.

If, indeed, degradation proceeds by a corrosion process, what can be done to retard or remove the problem? One possible solution may be to add a third intermediate layer between the Ti and Ag, and provided such a layer acts as a diffusion barrier, the underlying Ti would be protected. This solution has received some attention recently with Pd as the intermediate layer.[4] A second possibility is to provide a diffusion barrier over the entire Ti-Ag contact. For example, a SiO_2 or Al_2O_3 integral cover glass slide could be intimately bonded to the SiO antireflection layer and Ti-Ag contacts by sputtering. One problem does exist in that the ohmic strip contact needs to be exposed for soldering. Perhaps the cover glass slide could be deposited after attaching a lead to the strip contact or

even possibly after mounting cells on solar cell panels. Increasing the thickness of the Ag layer in Ti-Ag contacts would not be expected to retard degradation significantly, although it may help some. Finally, other metal contact combinations may prove more successful in this application.

SECTION VI

Bibliography

1. The Corrosion Handbook, Herbert H. Uhlig, John Wiley and Sons, Inc. 1948.

2. Corrosion and Corrosion Control, Herbert H. Uhlig, John Wiley and Sons, Inc. 1963.

3. Protective Coatings for Metals, R. M. Burns and W. W. Bradley, Reinhold Publishing Corporation. 1955.

4. H. Fisher and R. Gereth. New aspects for the choice of contact materials for silicon solar cells. Paper presented at 7th Voltaic Specialists Conference, JPL, Pasadena, Calif. Nov. 19-21, 1968. Elec. Dev. Group of IEEE.

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Figure 1 In (a), the structure noted on the grid line in the upper half of the micrograph is due to incomplete coverage of SiO. Magnification is 120X. In (b), the Ti-Ag ohmic strip contact is seen to be severely blistered. Magnification is 32X. 2

(a) (b)

Figure 2 Blisters developed in the central unmasked region of a Ti-Ag contact when placed in KOH but not in the adjacent masked region. This finding demonstrated that the Ag film is sufficiently porous to cause this attack. Magnification is ~ 0.75X. 8

Figure 3 In (a), blisters are noted on the ohmic strip contact after 3 days in NaCl solution. In (b), the same area, after 10 days, shows some blisters grew in size while new blisters formed. Magnification is 120X. 10

(a) (b)

Figure 4 An ohmic strip contact (a) before and (b) after immersion in KOH for 3 days. Magnification is 120X. 11

(a) (b)

Figure 5 An Auger spectrum showing Si (90 eV), B or Cl (183 eV), Ag (300 and 357 eV), and Ti (390 and 425 eV) was recorded in the Ag-Ti transition region. Primary electron energy was 1500 eV. 14

Figure 6 An Auger spectrum recorded from the interface of a peeled cell shows Ag, Ti, and O. Primary electron energy was 1500 eV. 15

Figure 7 An EMM micrograph of a sectioned solar cell in the vicinity of the p-n junction (a) under zero cell bias, (b) under 10 V reverse bias, and (c) under 10 V forward bias conditions. Magnification is ~100X. 18

(a) (b) (c)

Figure 8 An EMM micrograph of a sectioned cell in the vicinity of the Ti-Ag grid line (a) under zero bias, (b) under 10 V reverse bias, and (c) under 10 V forward bias conditions. 19

(a) (b) (c)
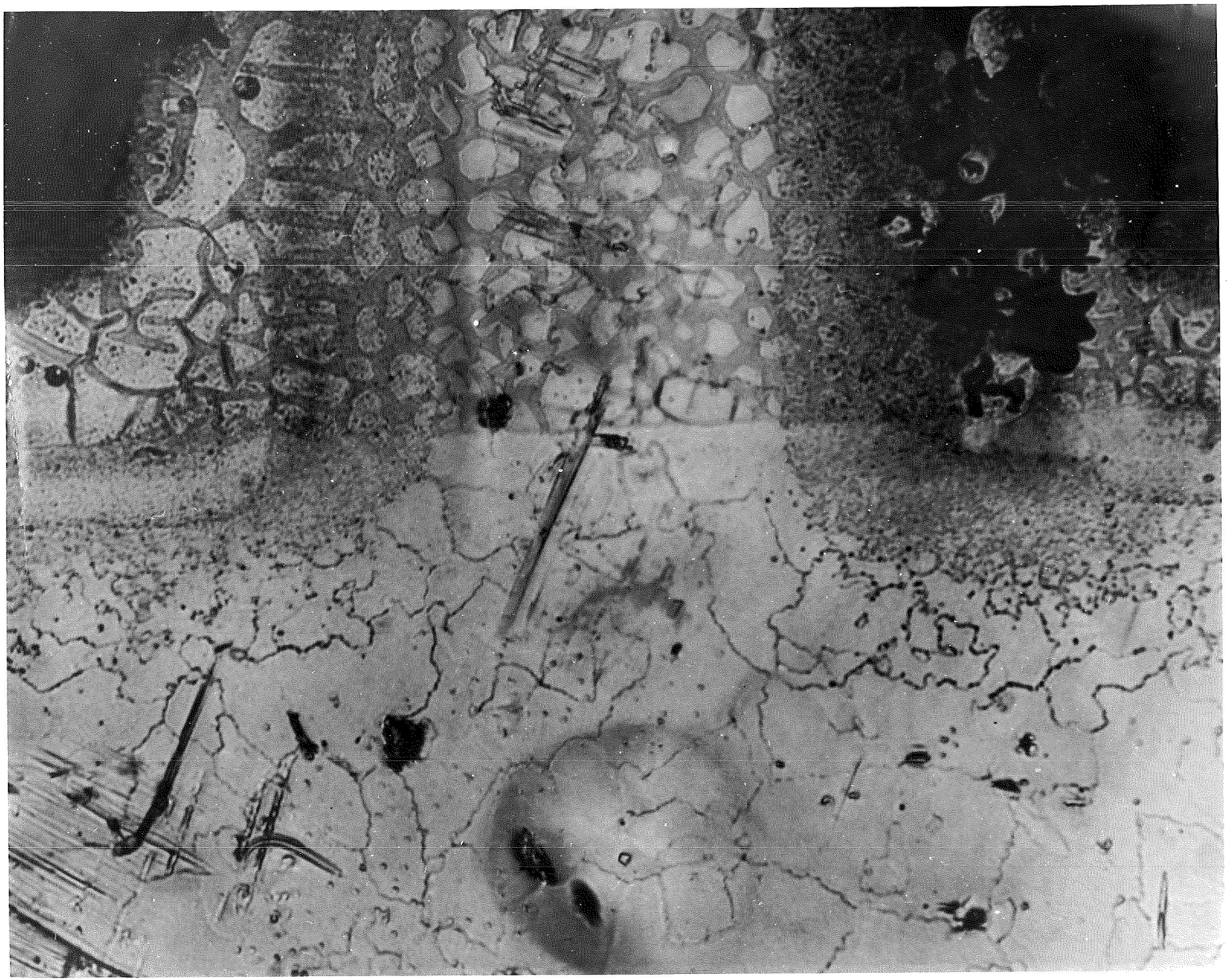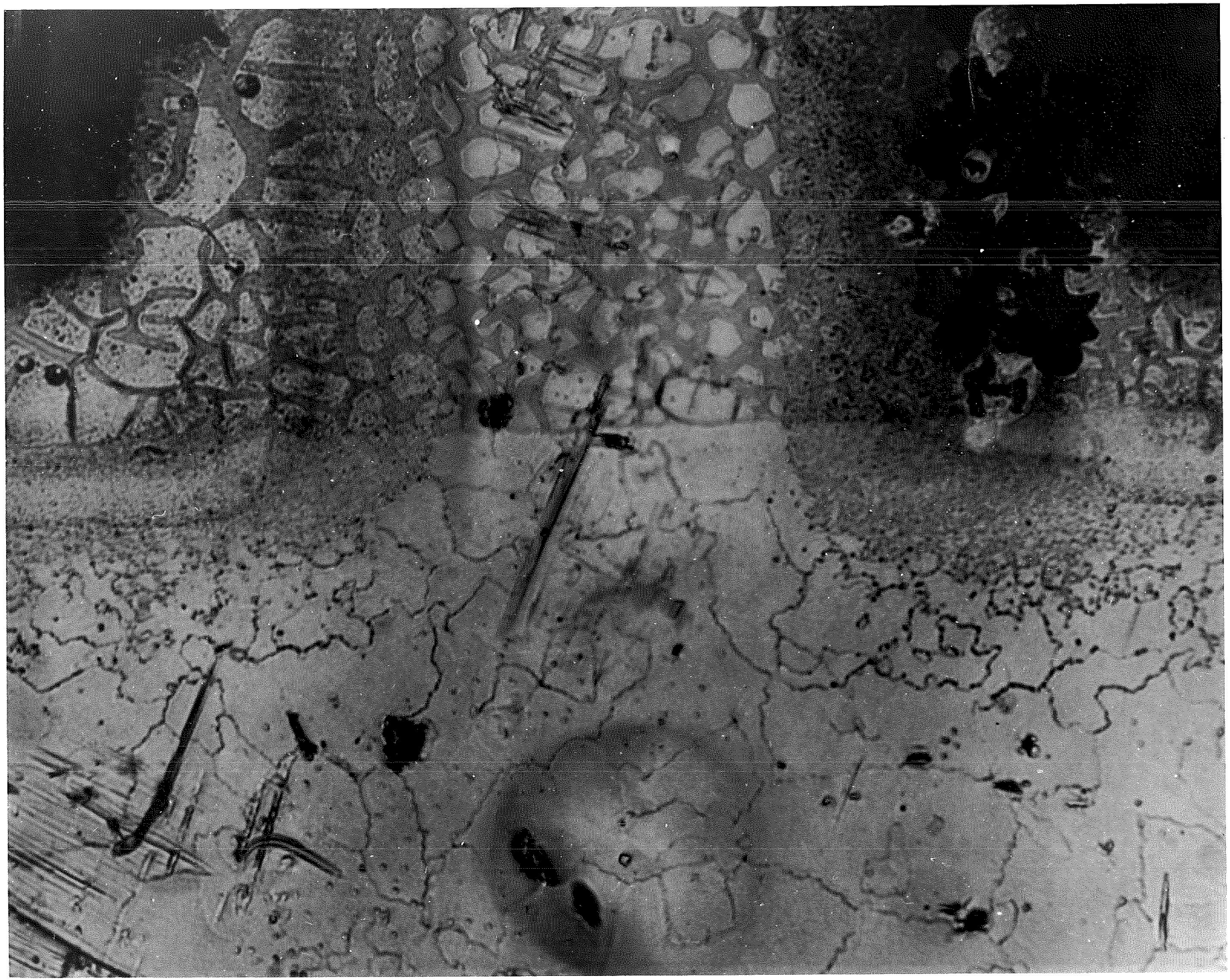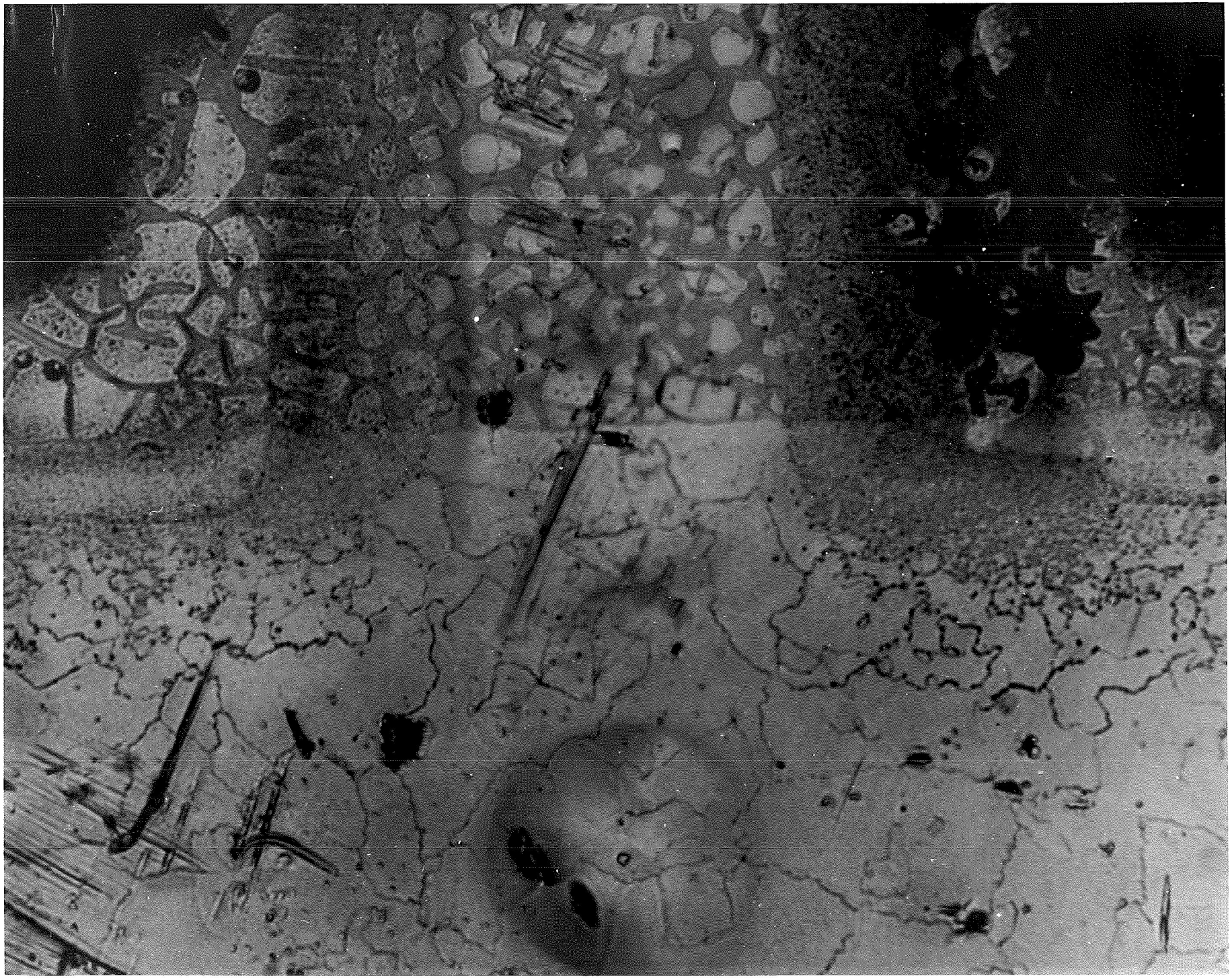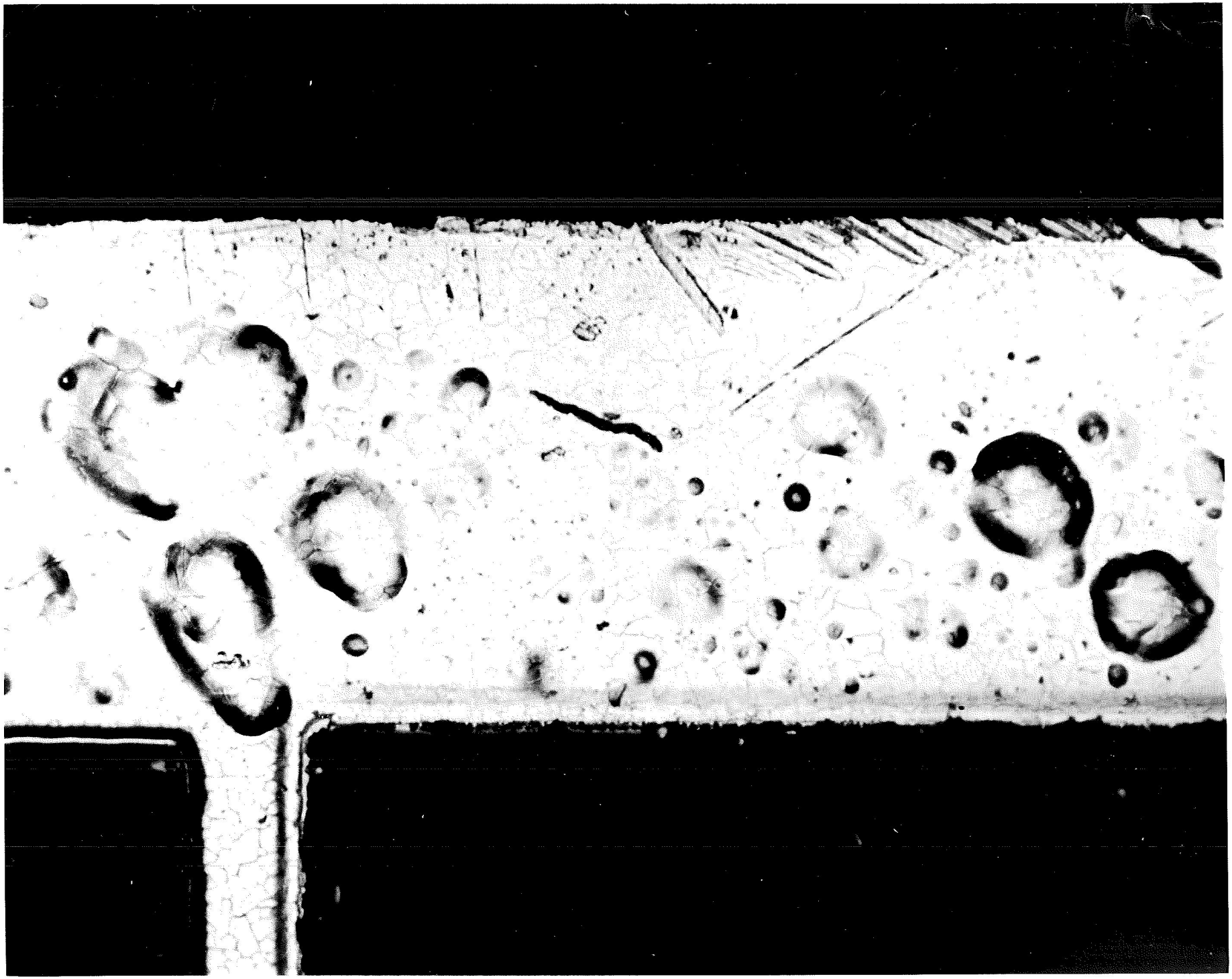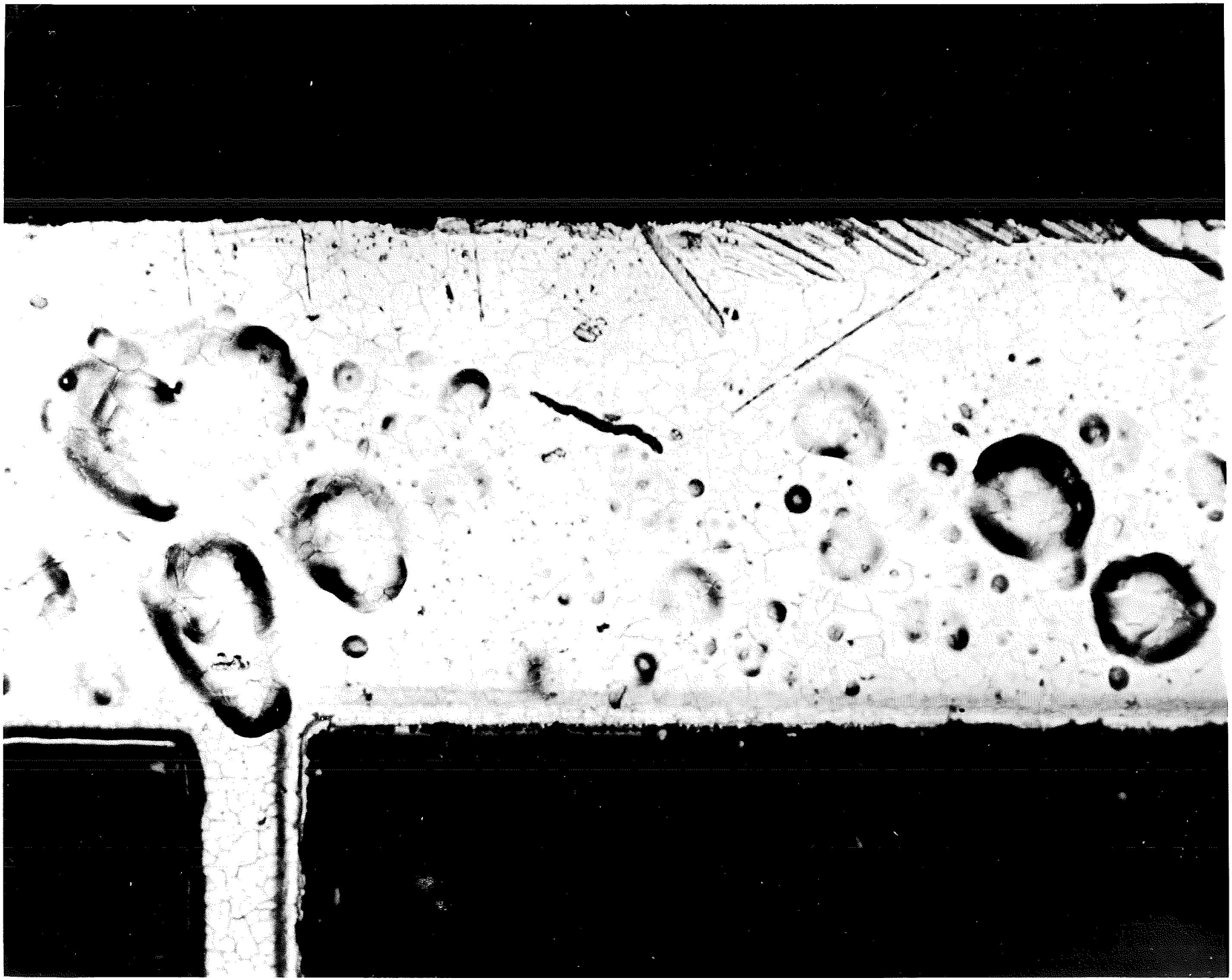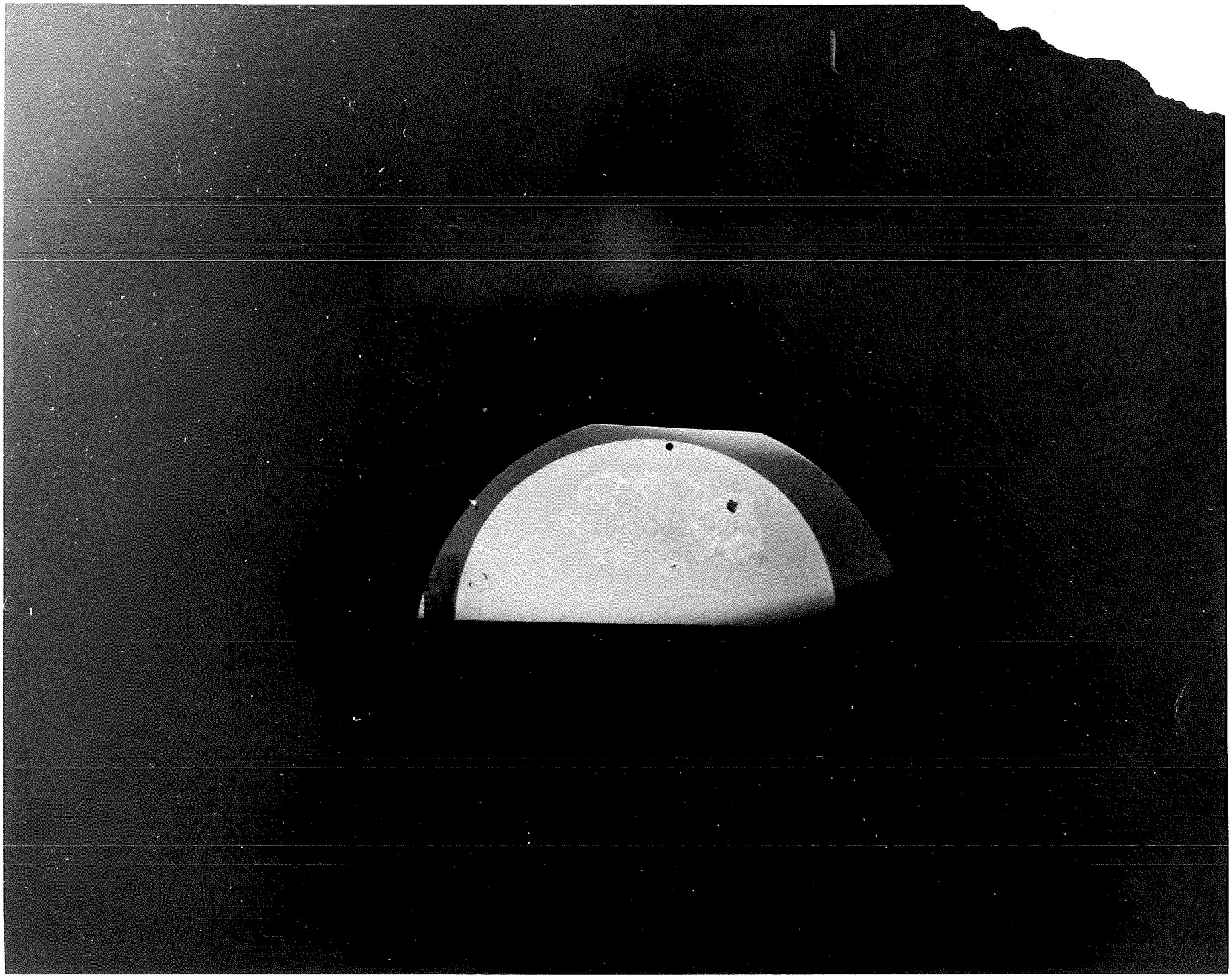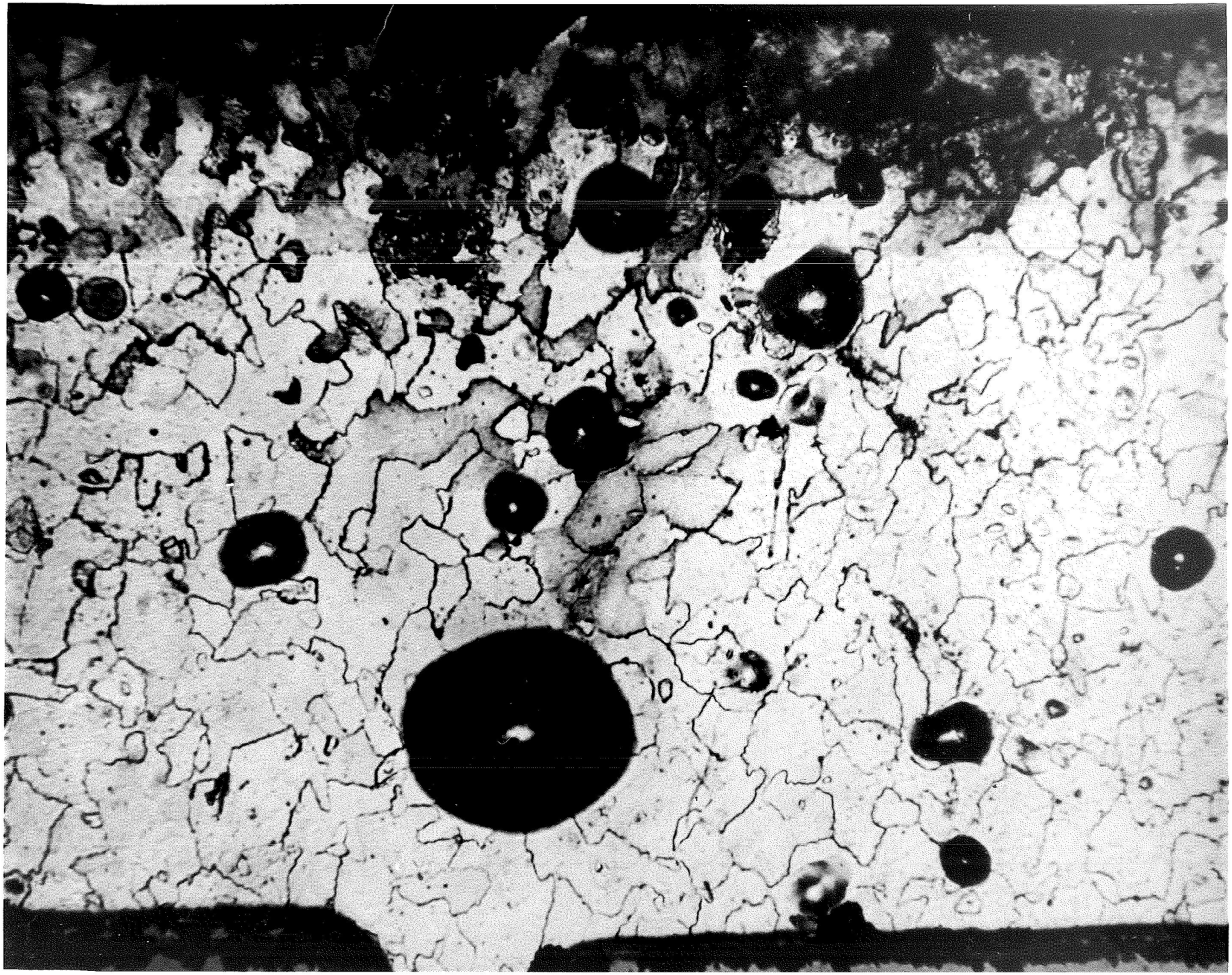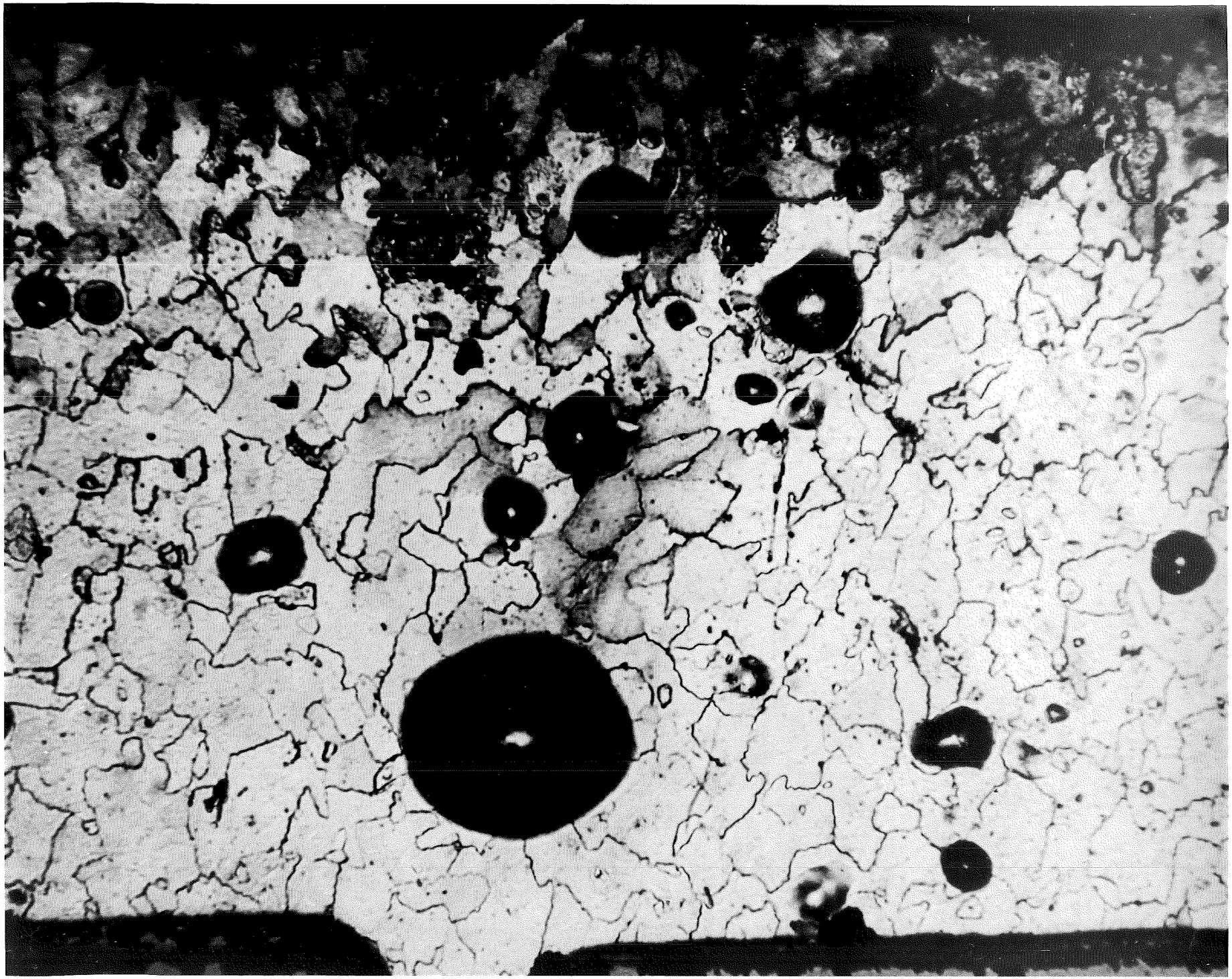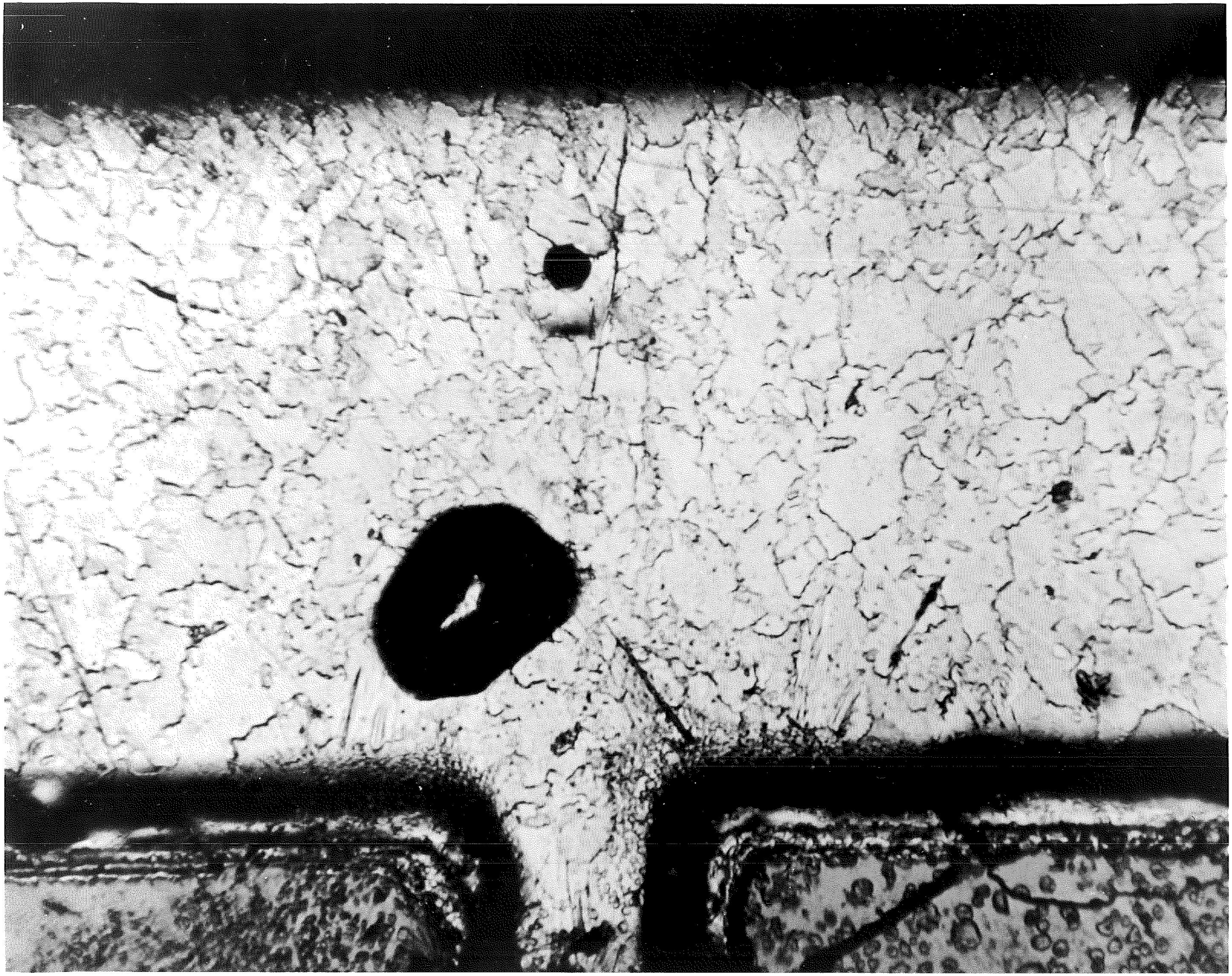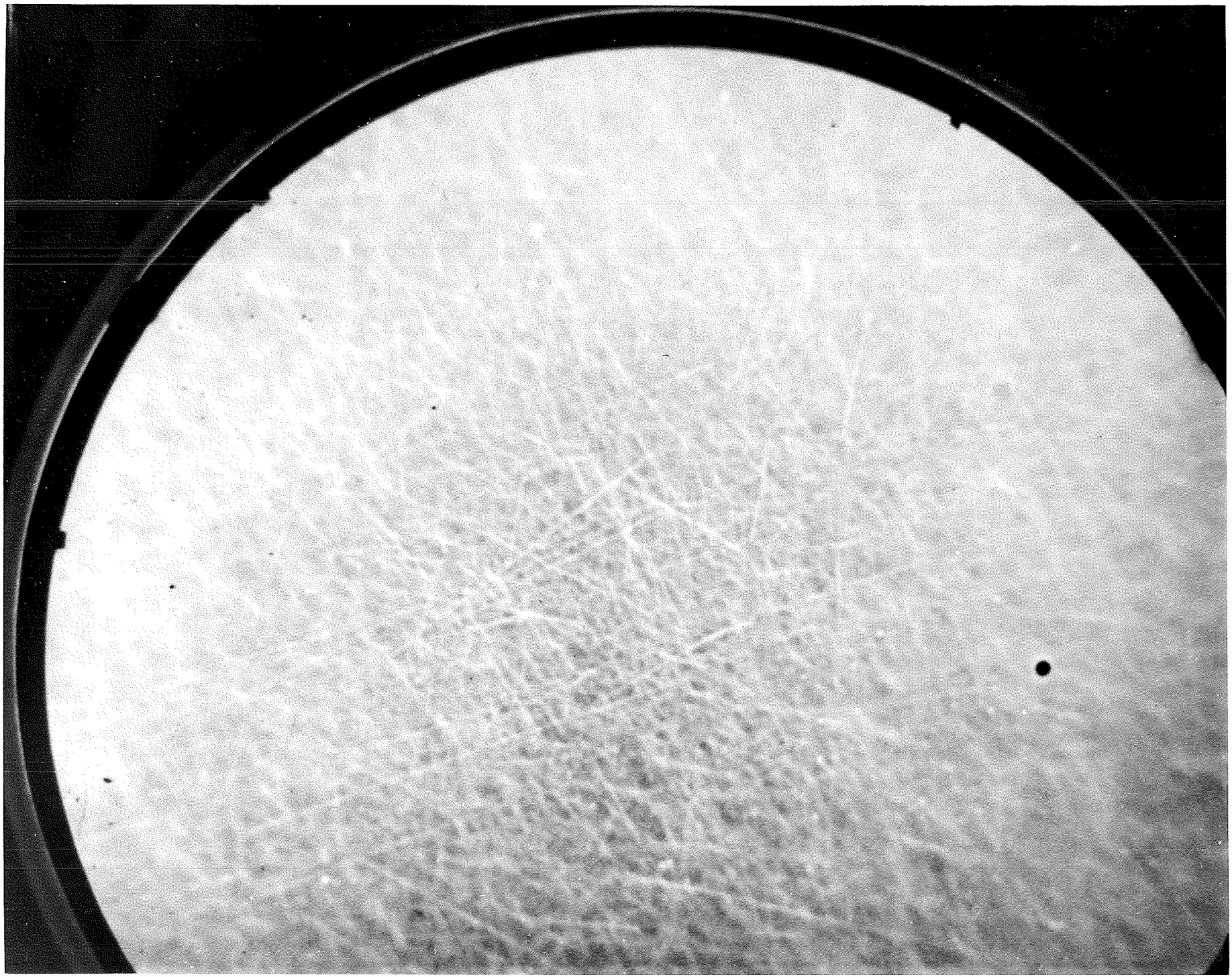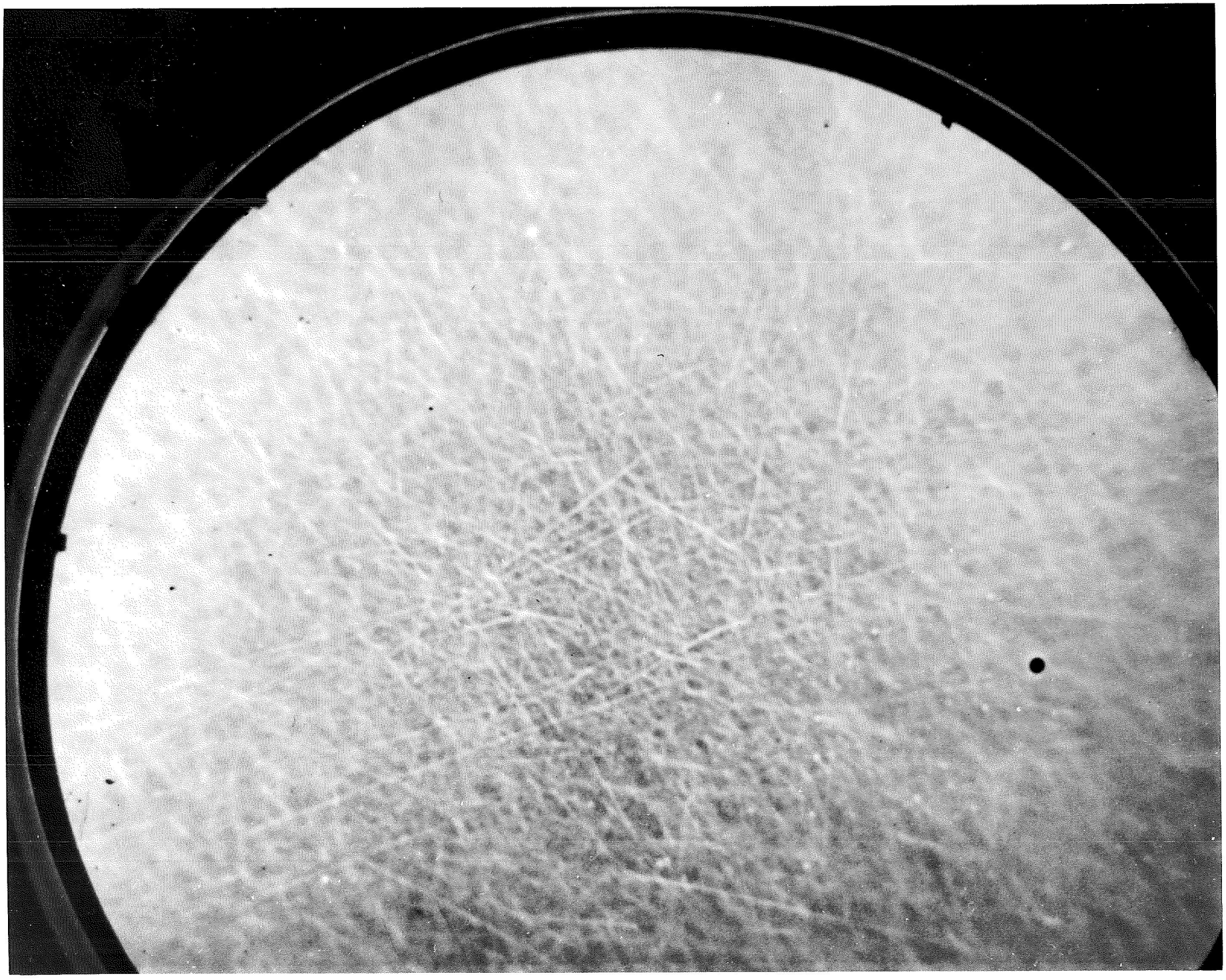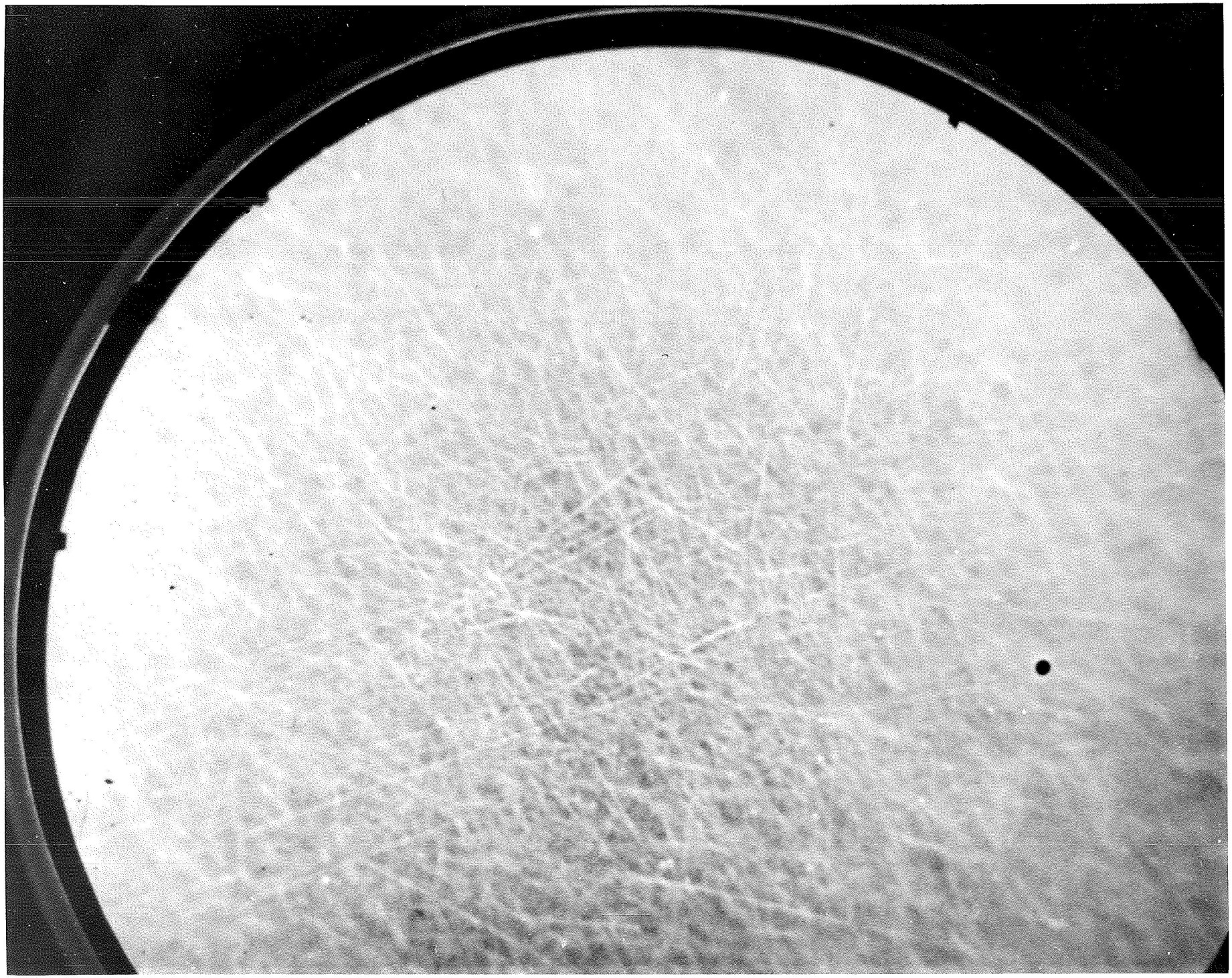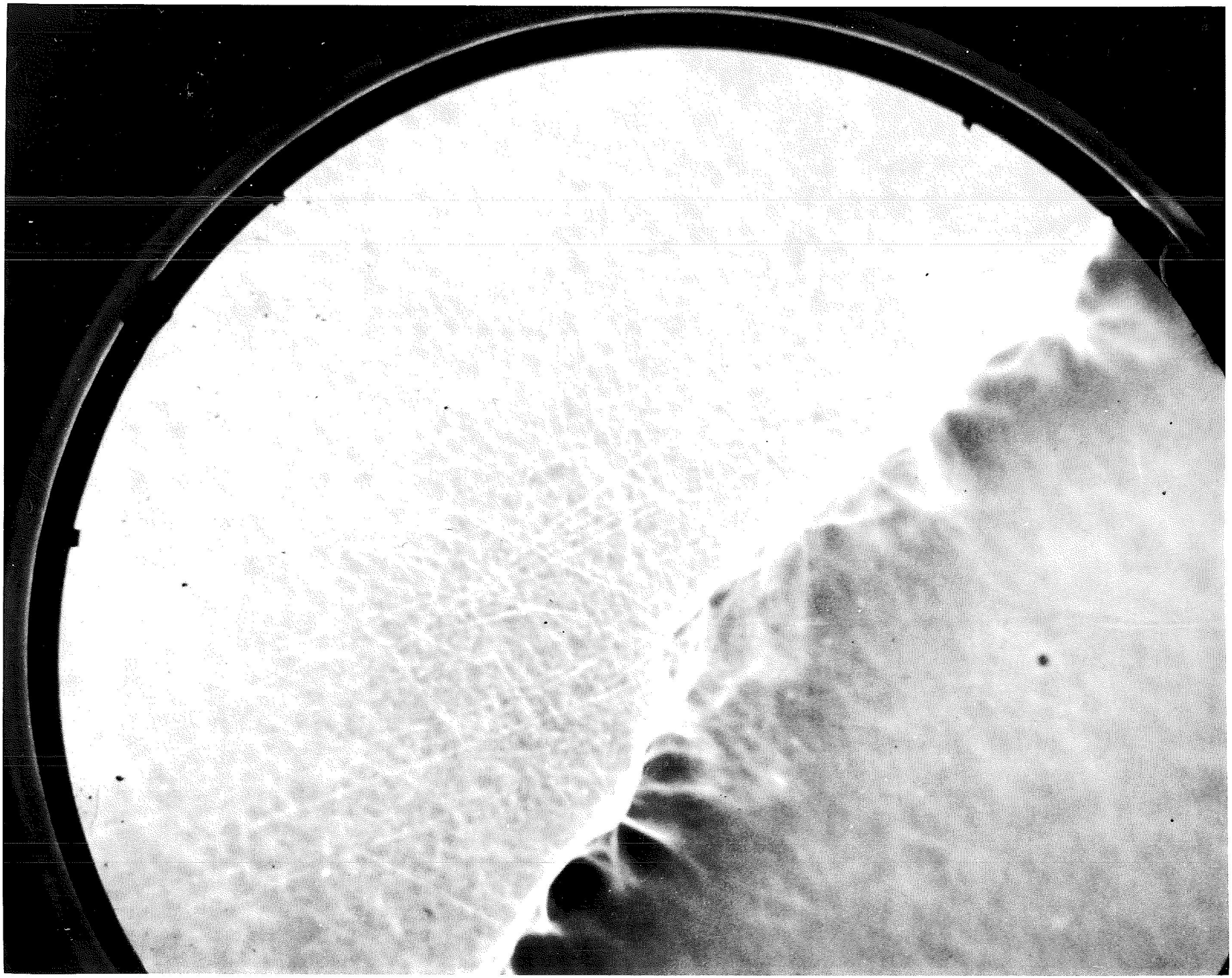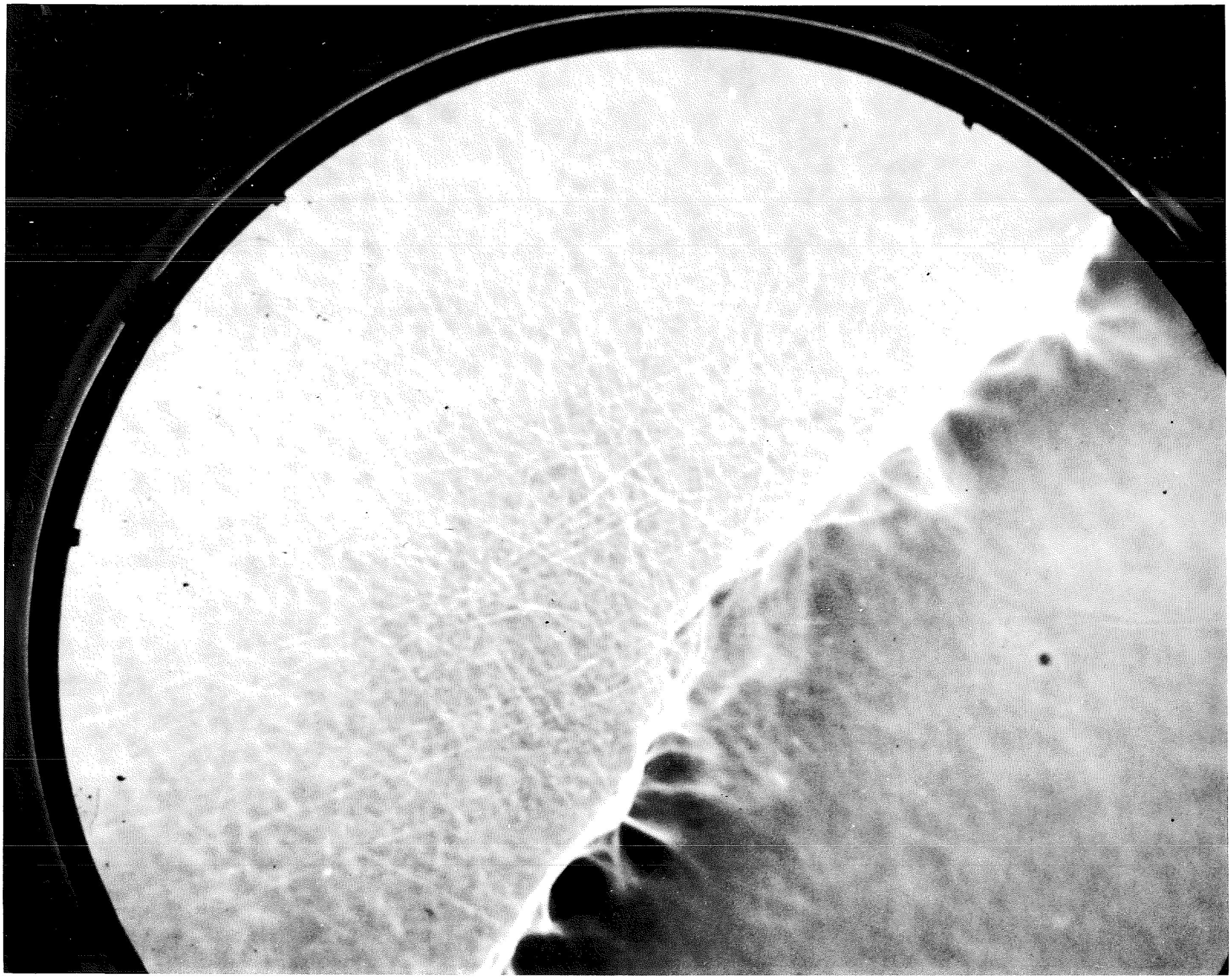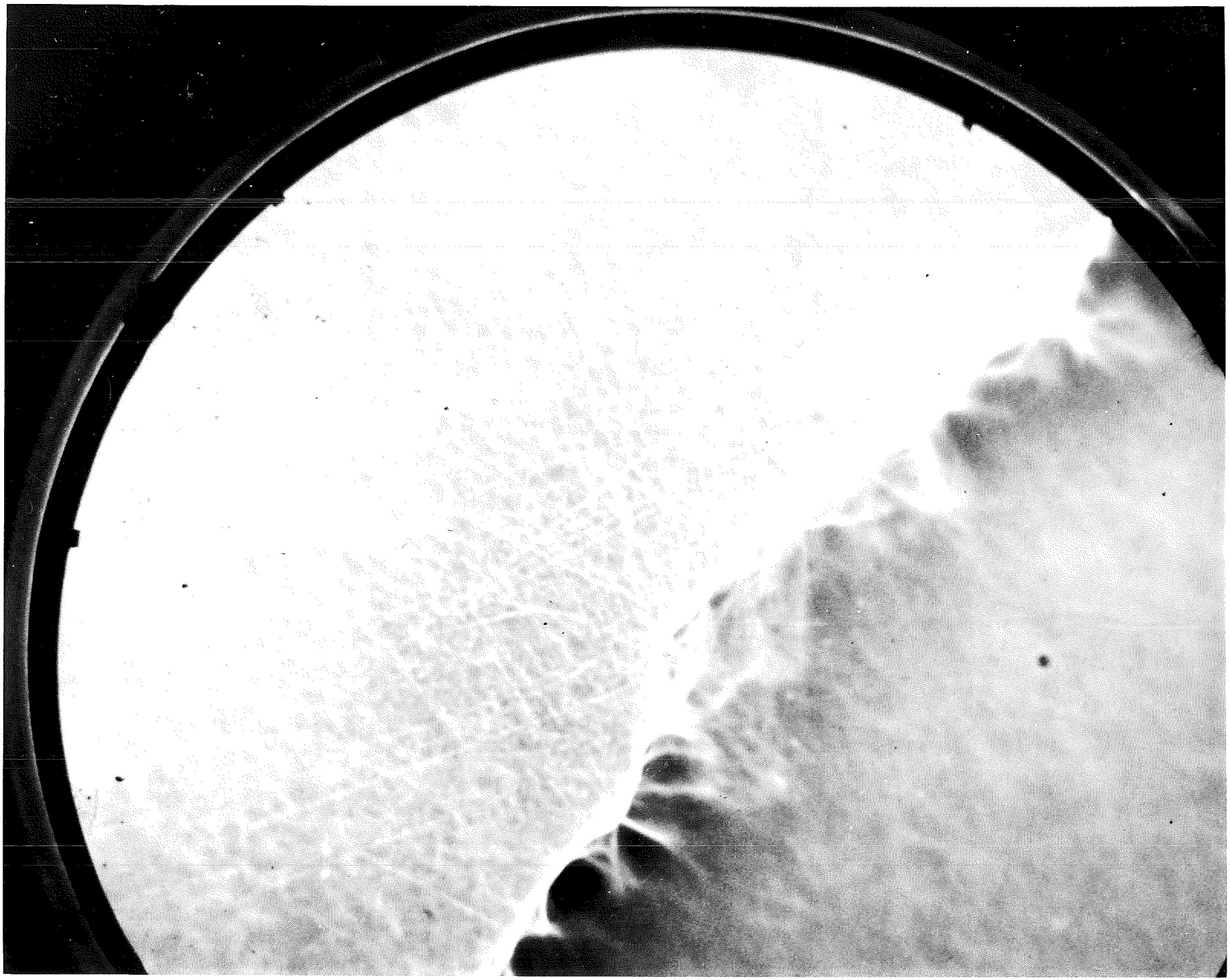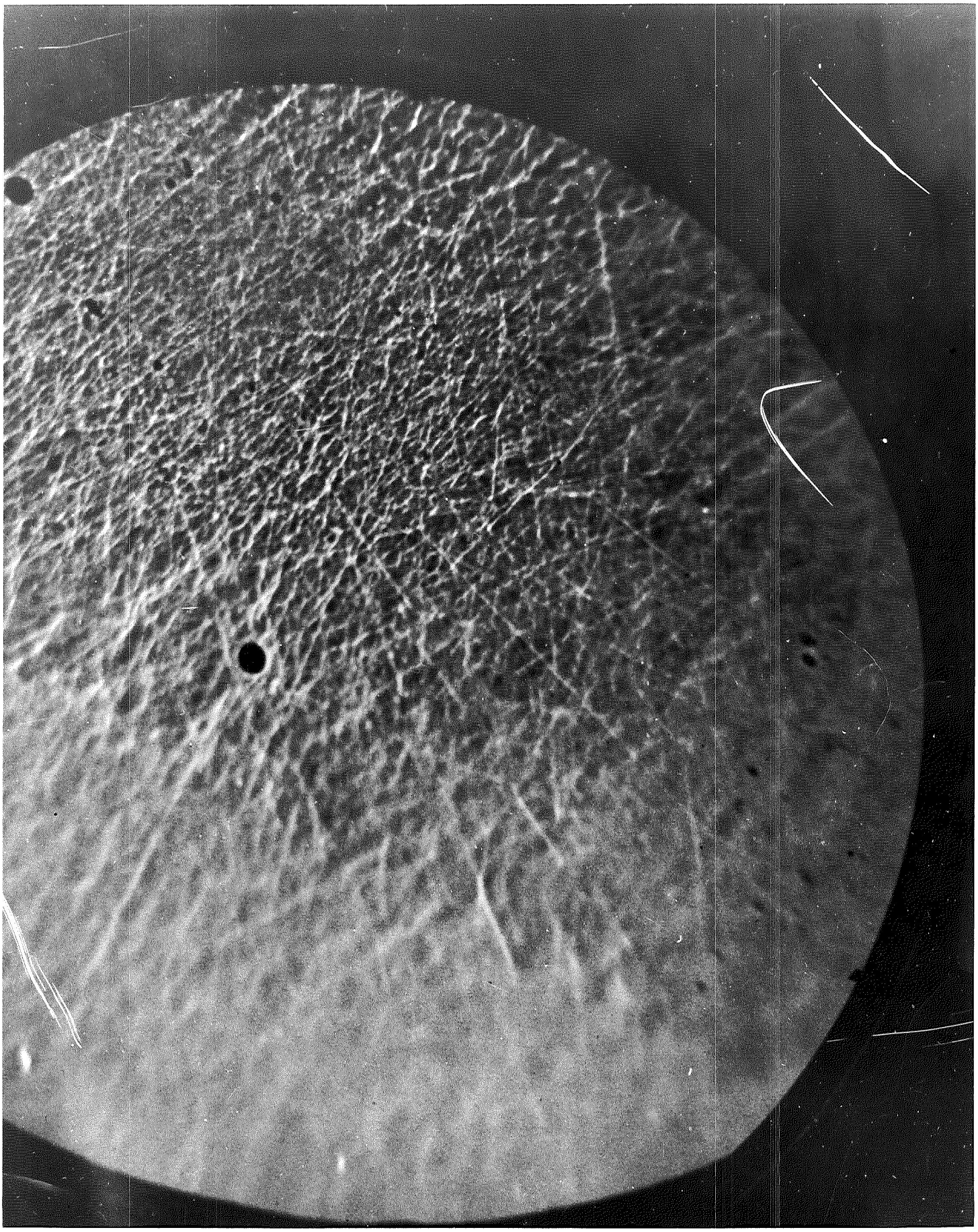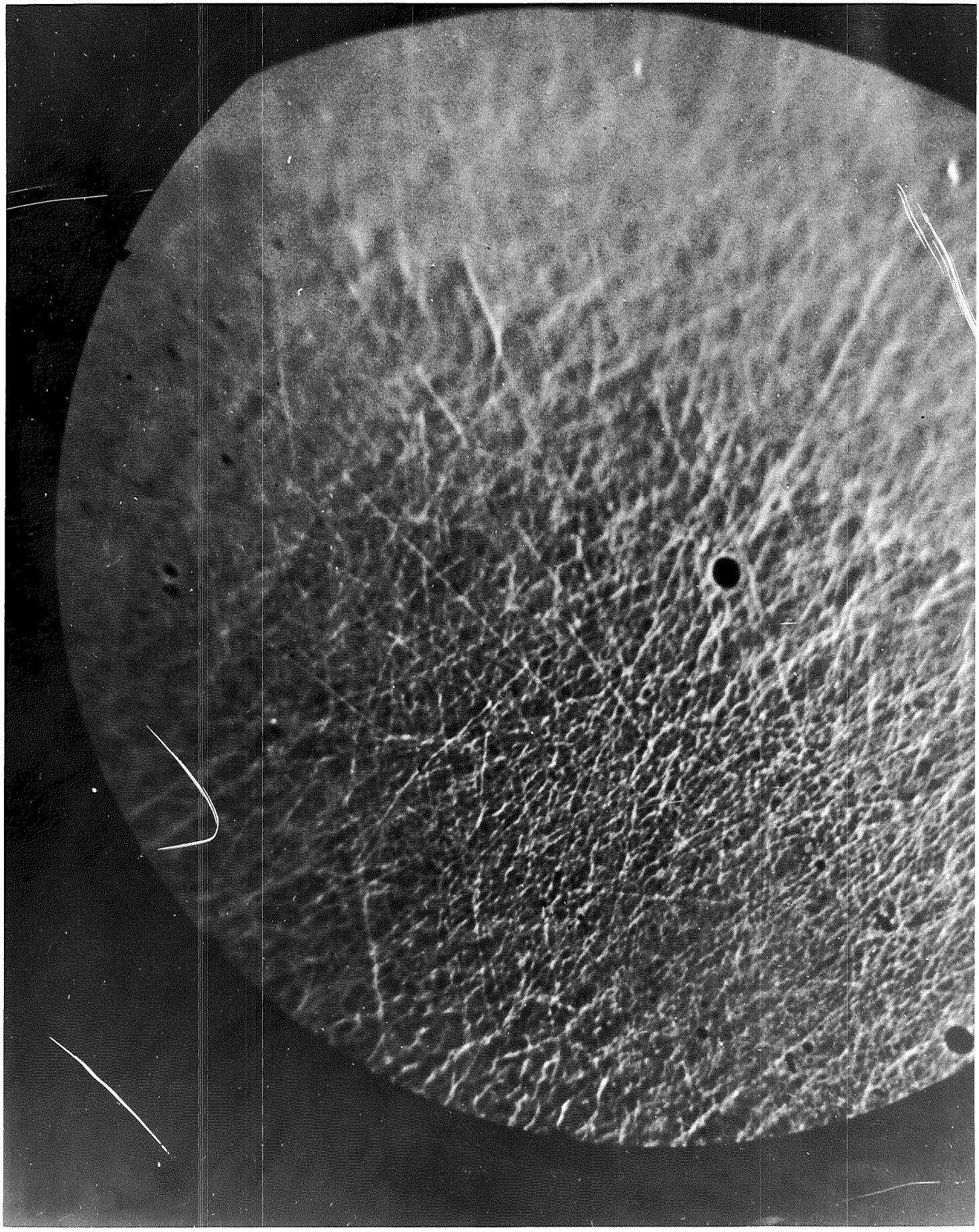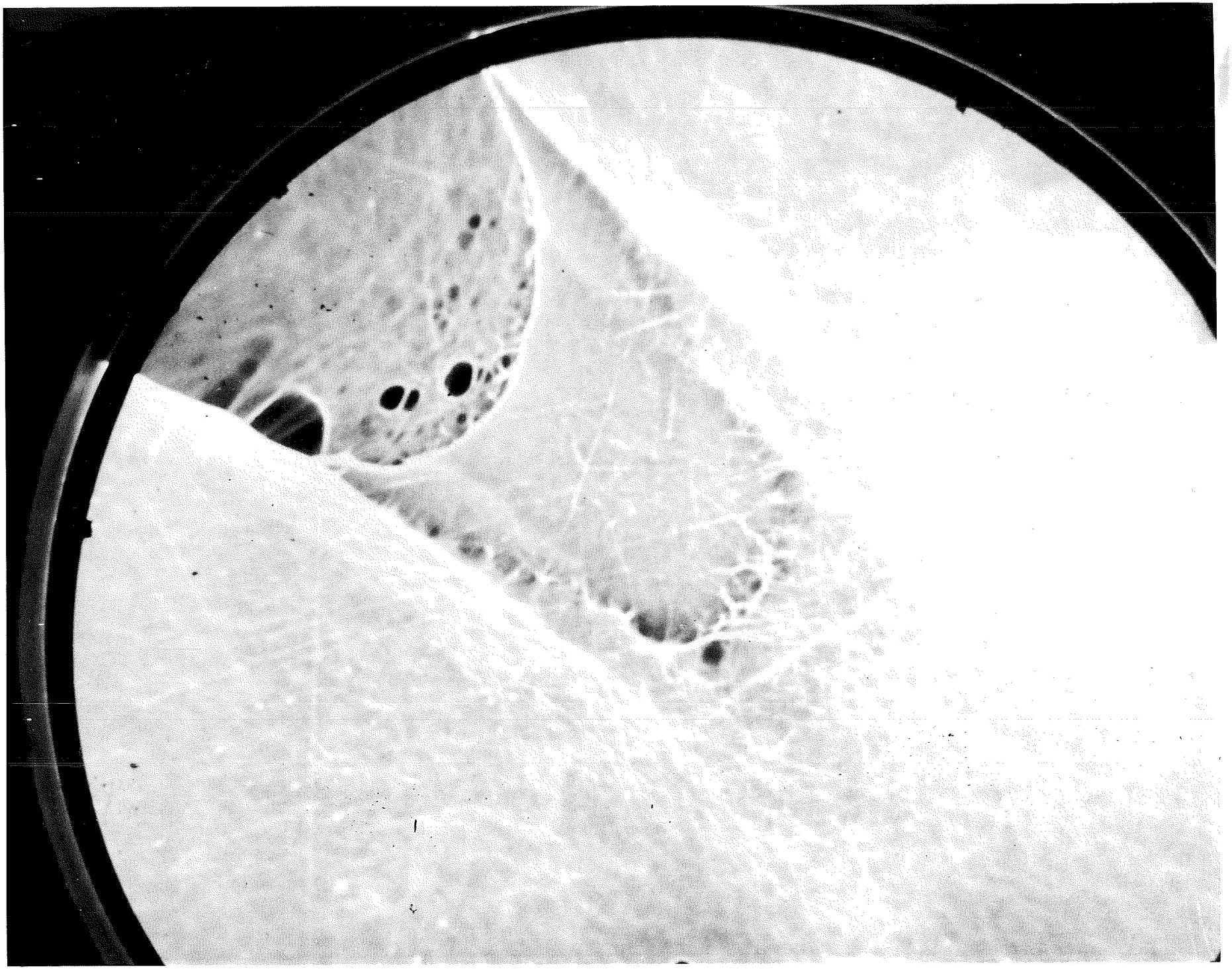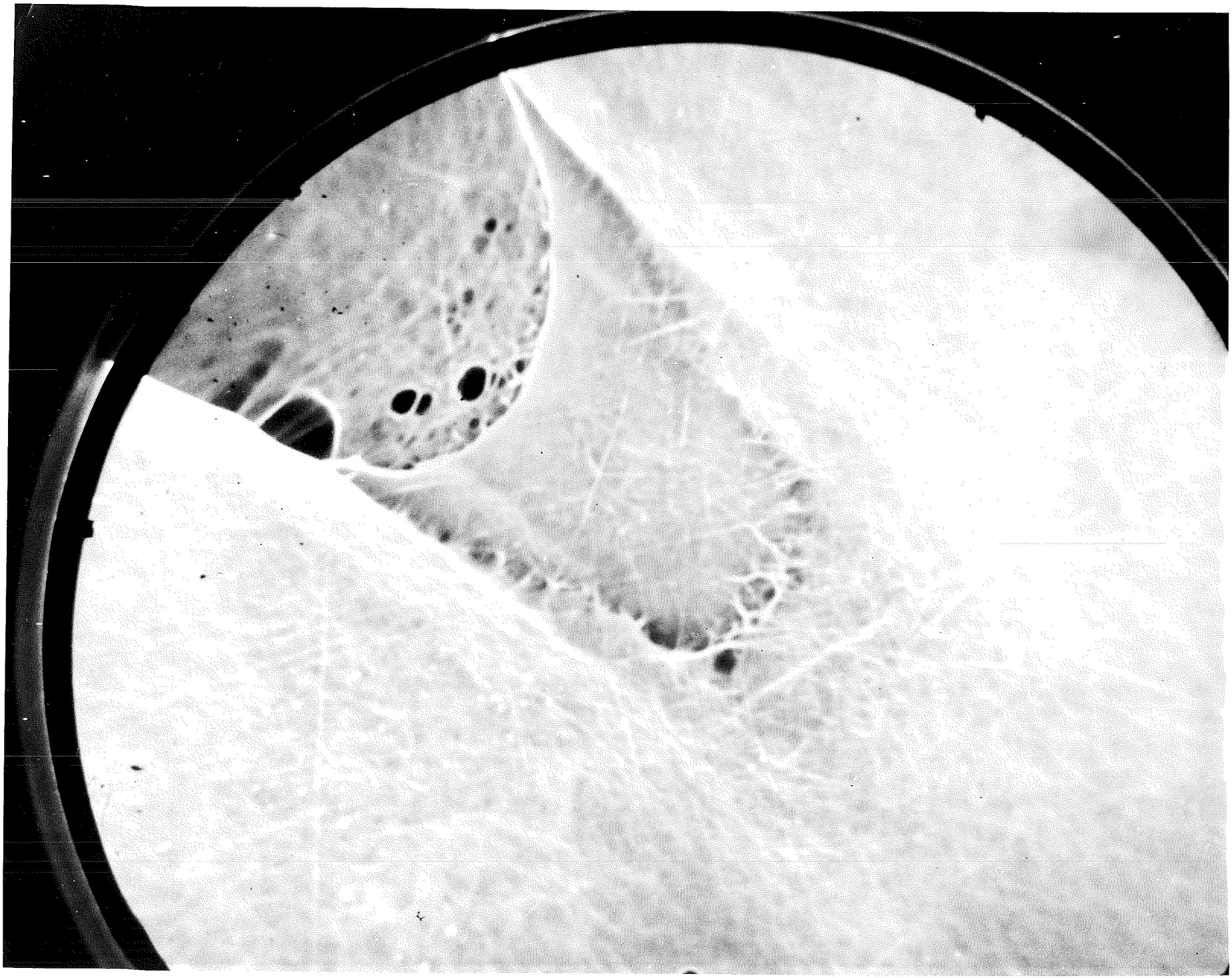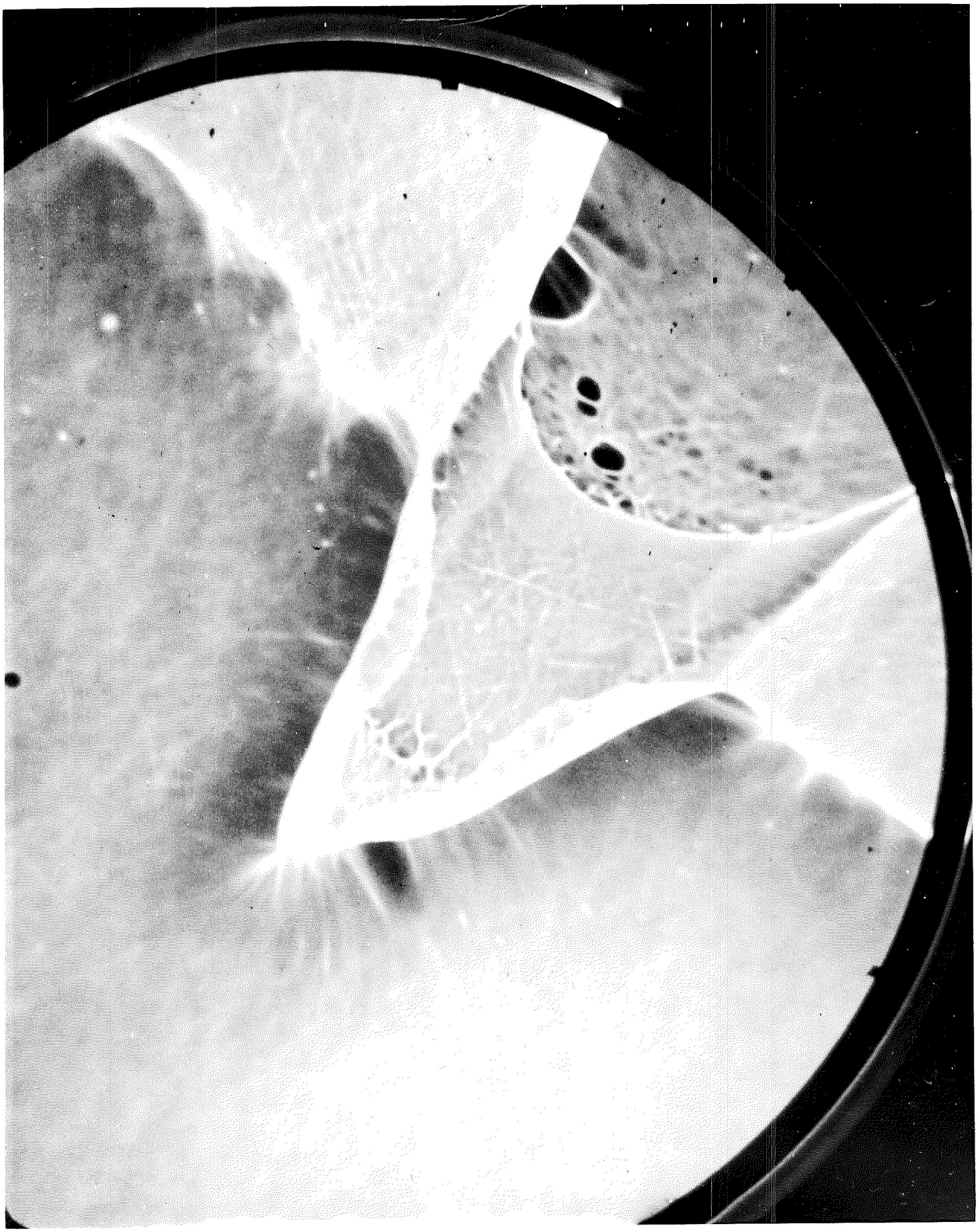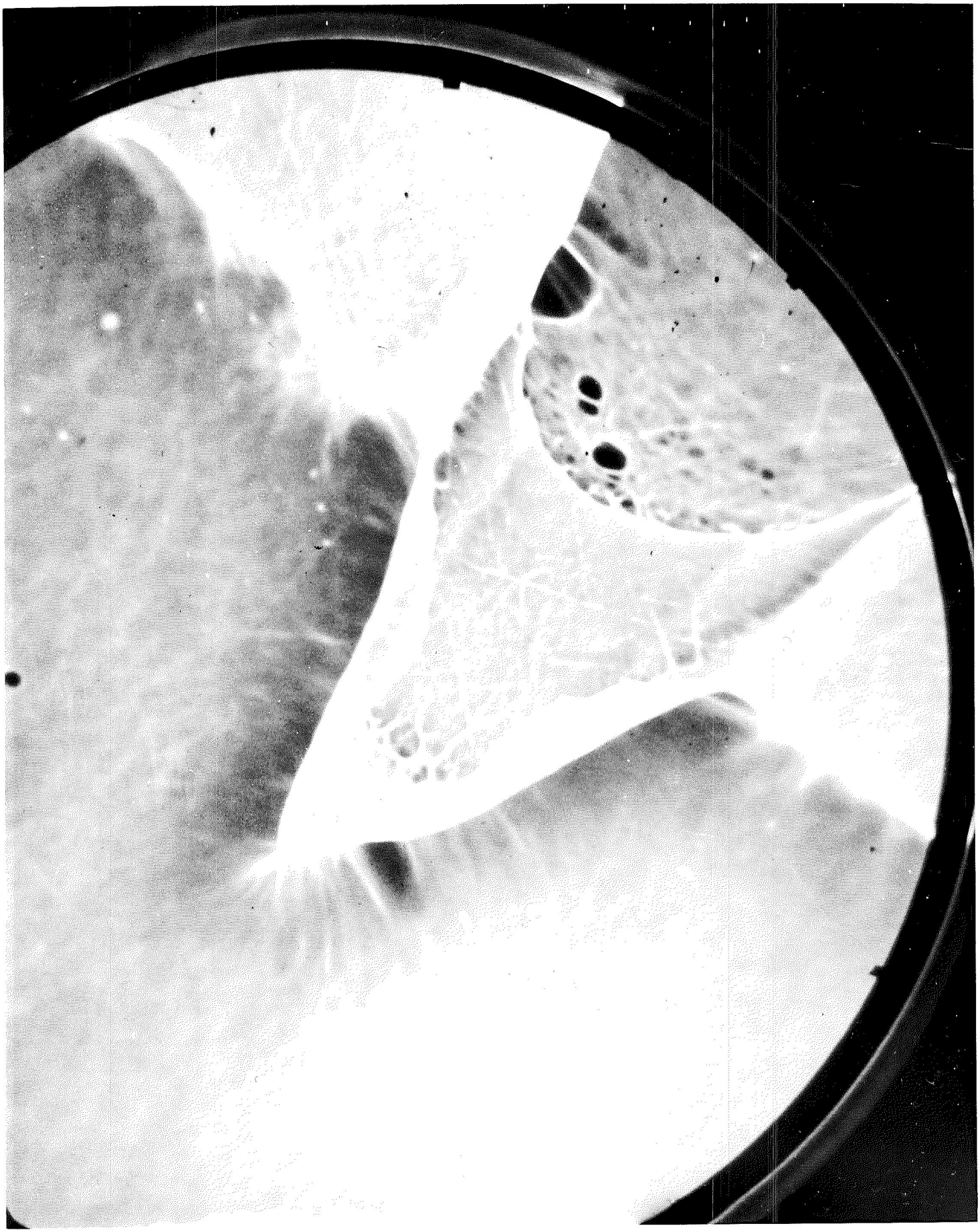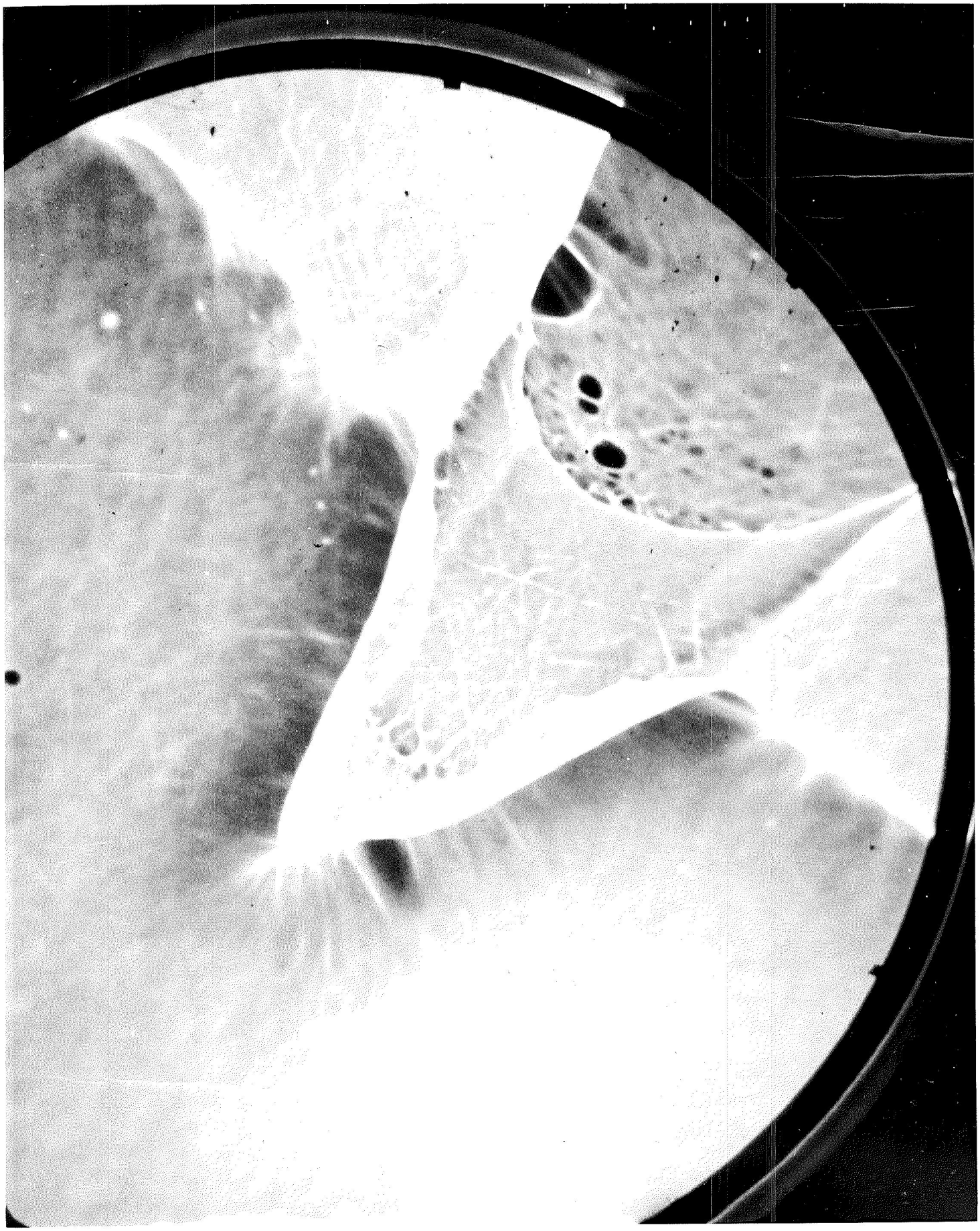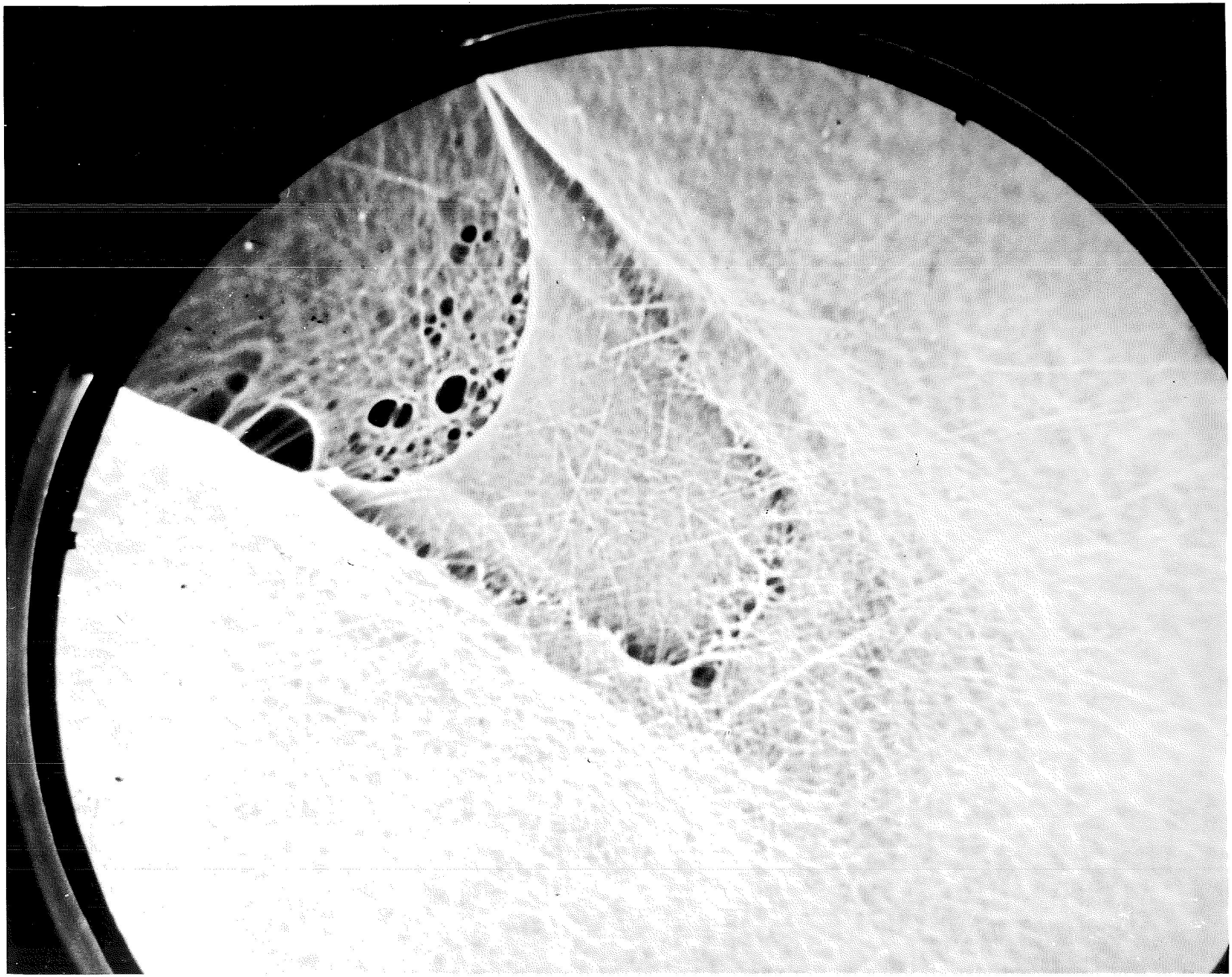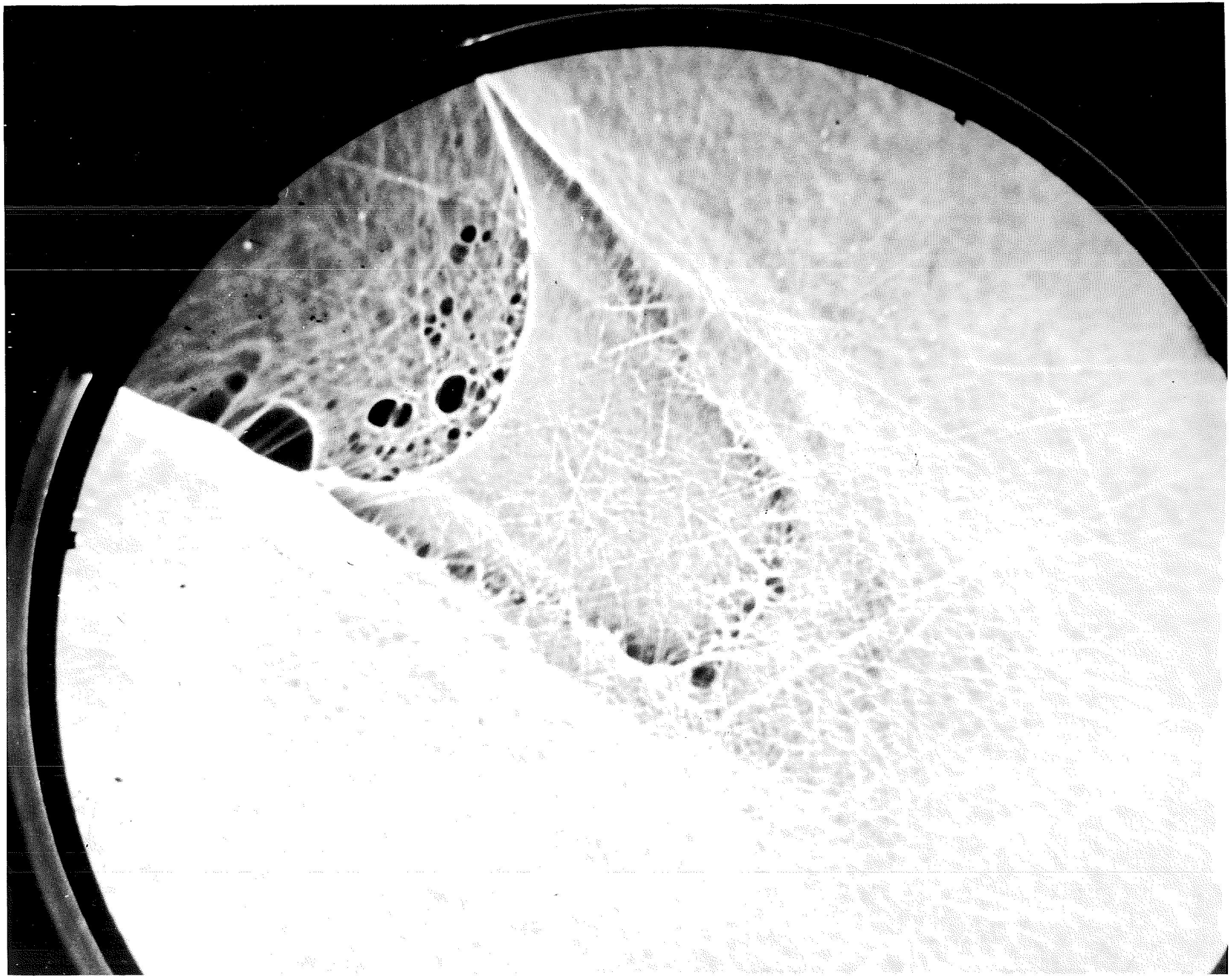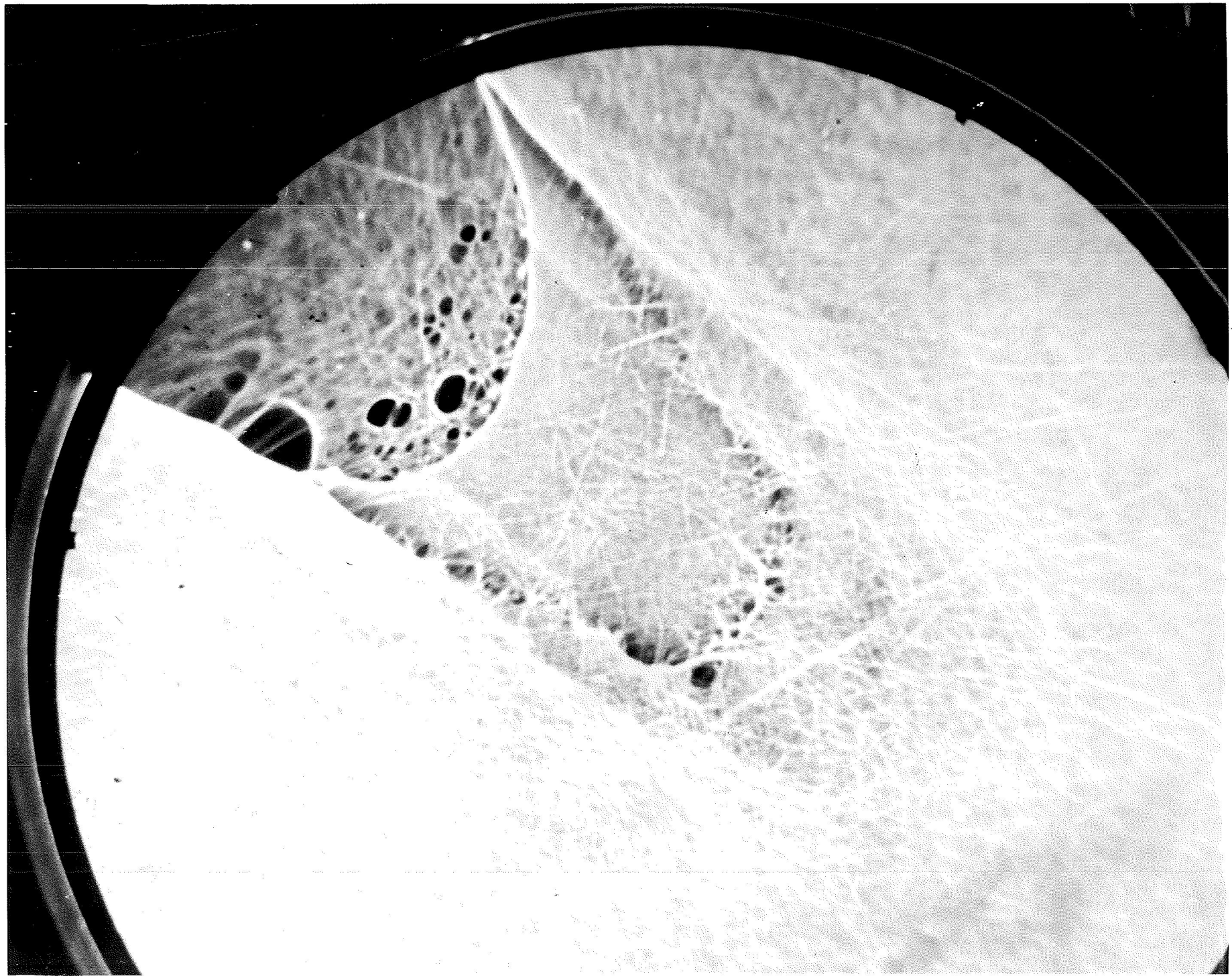
Figure 9 A potential profile of a sectioned solar cell in the region of the Ti-Ag grid line and p-n junction. A forward bias current of 1.0 A was flowing through the cell. 21